

DETECTION TECHNIQUES FOR TENUOUS PLANETARY ATMOSPHERES

Twenty-Second Six-Month Report
for the period
1 January 1974 to 30 June 1974

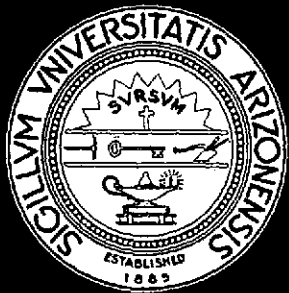
For the

National Aeronautics and Space Administration
Grant NGL-03-002-019

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COLLEGE OF ENGINEERING
THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA

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I. INTRODUCTION, ABSTRACT, AND SUMMARY

This report will cover the work performed from 1 January 1974 through 30 June 1974 on Grant NGL 03-002-019 between the University of Arizona and the National Aeronautics and Space Administration.

This contract was set up to support the development of new types of detectors for analysis of planetary atmospheres. Initially, the interest was in detectors for use under partial vacuum conditions; recently, the program has been extended to include detectors for use at one atmosphere and adsorption systems for control and separation of gases.

Results to date have included detectors for O_2 and H_2 under partial vacuum conditions (publications 1, 3, 4). Experiments on detectors for use at high pressures began in 1966; and systems for CO , H_2 , and O_2 were reported in 1967 and 1968 (publications 8, 11). In 1968 studies began on an electrically controlled adsorbent. It was demonstrated that under proper conditions a thin film of semiconductor material could be electrically cycled to adsorb and desorb a specific gas. This work was extended to obtain quantitative data on the use of semiconductors as controllable adsorbents (publications 11, 12).

In 1968 a new technique for dry replication and measurement of the thickness of thin films was developed. A commercial material, Press-O-Film, was shown to be satisfactory when properly used. This technique is most useful for studies of semiconductor thin films where normal interference techniques are not practical because of the non-reflective nature of the film (publication 13).

During the period from 1968 through 1971 the Carbon Monoxide Detector, first demonstrated on the NASA program (publication 8), was refined and improved for use by the Department of Health, Education and Welfare.

In 1969 studies began on a Corona Discharge Detector for water vapor. This system was shown to be rapid in response, suitable for continuous operation, and reasonably linear in output (on a logarithmic plot) from 10 percent relative humidity to 95 percent relative humidity. A program to develop this detector for hydrological applications began in 1970 but was temporarily dropped because of limited user interest.

In 1970 we began an investigation of the catalytic oxidation of various gases, i.e., CO, NH₃ and H₂ over metallic catalysts. We demonstrated that the rate of reaction could be observed and controlled in terms of the exoelectron emission from the catalyst (publication 16). In 1971 this study was directed to the extended monel metal catalysts used for auto exhaust emission control and for spacecraft atmospheric purification (publication 20).

In 1971 we began the study of a new technique for analysis of solid materials. This system involved heating or grinding the substance and observing the induced exoelectron emission. This effect is known as Temperature Stimulated Exoelectron Emission (TSEE). One application of this phenomenon to observation of grinding processes has been published (publication 18).

Other applications of the exoelectron phenomenon to dust levitation and industrial health are under study at the present time. There may be a direct correlation between the exoelectron emission we observe, after grinding, and the effect of the ground silica on red blood cells.

II. SUMMARY OF WORK IN THE PAST SIX MONTHS

A. Catalytic Studies

The original program involved a demonstration that exoelectron emission could be used to monitor and partially control the rate of a catalytic reaction; the details of the work have appeared in the literature (publication 16). We have expanded this work to demonstrate that the technique can be used to monitor the monel catalyst that is used for automotive smog reduction. A Letter to the Editor discussing this work has appeared in the *Journal of the Society of Automotive Engineers* (publication 20).

In the past six-month period we have begun a series of studies of catalytic reactions at atmospheric pressure. The rationale for this

is twofold; first we want to demonstrate that EEE can be used to monitor catalytic reactions at atmospheric pressure. Another area of interest is the application of our catalyst monitoring system to the smog burners used in submarines and spacecraft for control of carbon monoxide. If progressive failure of the catalyst is not detected early, the mission may have to be aborted because of the buildup of CO in the vehicle environment.

The experimental apparatus used for this study is shown in the attached Figure 1. Air is drawn in by a fan and mixed with the gas under study (the mixture ratio is held below the explosive limit by a series of precision flowmeters). The mixture is sampled by the mass spectrometer and allowed to pass over the catalyst. The EEE from the catalyst is monitored by the usual battery and picoammeter system. The gas mixture is sampled again, after reaction, to determine the reaction constant for the system.

Experiments to date have made use of an electrically heated palladium catalyst. The catalyst is wound on a ceramic support and a thermocouple is positioned for temperature control. The catalyst is heated by AC current via a transformer. The catalyst can be held at DC ground or floated for observation of EEE effects.

Typical results with CO/air mixtures are shown in Figure 2 where we have plotted the EEE current versus catalyst temperature for a series of CO/air mixture ratios. There is a definite correlation between the temperature, mixture ratio and EEE current in agreement with the results reported earlier in publication 16.

Similar results with methane/air mixtures are shown in Figure 3. These experiments were complicated by our use of natural gas, from the El Paso Gas Co., as a source of methane. Natural gas is 99% methane with the remainder being complex hydrocarbons of the ethane series. These gases have no odor and mercaptans are added to alert citizens to leaking gas. The mercaptans contain sulfur and have periodically poisoned our catalyst when the gas/air ratio exceeded 2%. We have added a charcoal filter to the system to remove mercaptans and the data of Figure 3 was taken with filtered gas. Once again there is a clear and reproducible relationship between the mixture ratio, catalyst temperature and EEE current.

In the next six-month period we plan to repair the mass spectrometer (parts have been ordered) and obtain correlations between the EEE currents shown in Figures 2 and 3 and the rate of reaction of the gas/air mixtures. This will settle any question of the application of EEE to monitoring catalysis and should serve to encourage industrial applications. We have discussed possible uses of this system with representatives of the Dow Chemical Co. and S. A. Hoenig will visit the Dow Chemical facility in Freeport, Texas in July 1974.

Another area of interest involves the use of EEE for observation of catalytic reactions on supported catalysts. Our first studies will make use of Hopcalite since it is the catalyst used for CO removal in spacecraft. It will be most interesting to see how these low conductivity materials behave during catalytic reactions.

A long-term interest exists in the mechanism of catalysis itself and to study this we propose to use a strip of palladium on which lines of known width have been scribed. The scribe marks will be monitored during the catalytic reaction by a microscope and a 35mm camera. We hope to relate the smoothing-out of the scribe marks to the motion of vacancies on the catalyst by the methods of references 1 and 2. Since vacancy motion is known to result in EEE we will have two techniques for observing the process and relating it to the rate of reaction.

B. Dust Grinding and Electrification Studies

In the last six months a major effort has been devoted to the development of instrumentation for analyzing the charge that appears on dust after grinding. We felt that size effects might be significant in this process and modified a commercial impaction sampler to allow a measurement of the charge on the dust after separation has taken place.

The system developed for this purpose is shown in the attached Figure 3. In a typical experiment a measured quantity of material is ground and then sucked into the sampler by a vacuum pump. After separation is complete the pump is shut off and the sequential readings are taken of the dust charge at four levels in the sampler. Typical results of this work are shown in the attached Figures 4, 5, 6, 7, 8, 9, 10 and 11. The specimens for this study were provided by Mr. John Cable of the NIOSH laboratories in Cincinnati, Ohio as examples of common industrial-geological materials.

Examining these figures, it is interesting to note that in every case but one, the 1 micron (respirable fraction) is negatively charged while the larger dust particles are either positive or neutral, (magnetite is the exception). These experiments suggest that there is a significant variation in particle charge as a function of size. Similar results were reported by Loeb³, based upon the work of Kunkel⁴. In Kunkel's experiments ground silica flowed into a silica or platinum cup and then into the charge measurement system. With pure silica and a silica cup the dust was essentially neutral at all size levels. With a platinum cup there was an excess of negative charge, especially at the smaller sizes (1 micron). Our work, with typical industrial materials, suggests an even larger difference between the charge on the small and the large dust particles. We suggest that this is due to impurities but this question will require more study before it can be answered.

In other studies we have examined the charge decay of the respirable material after grinding. The results are shown in the attached Figure 12, for silica alone, and in Figure 13 for a series of other materials. It is clear in Figure 12 that the charge on the 1 micron silica is quite stable and electrostatic effects can be expected for some time after grinding. The decay of other materials (Figure 13) is more rapid, with the exception of foundry dust. This may be due to the presence of nonmagnetic iron in the foundry dust. Magnetite is, of course, highly magnetic but our tests with a small magnet indicated no magnetic effects in foundry dust. This is most interesting and will be the subject of further research.

Other data showing the effects of added iron or aluminum on the decay of the silica charge is attached, Figure 14. We observe that iron produced a large initial charge which decayed rapidly. Aluminum produced an even more rapid decay which may be connected with the prophylactic effect of aluminum for reduction of silicotic injury⁵. We are investigating these dust charging effects with the hope of developing a method for removing respirable dusts from industrial environments. This work will be supported by another organization but the overlap between the two programs will be of mutual advantage.

The experimental system that will be used for the dust levitation studies is shown schematically in the attached Figure 15. This system will allow us to observe levitation process and to sample the dust at various levels for charge measurement. We hope to determine the degree of levitation that might be expected under typical atmospheric conditions. If the results are favorable, we will use a vacuum system to simulate the atmospheric conditions on Mars.

The charged fog generator, shown in Figure 15, will be supplied by another organization and will be used for the dust removal studies. In that work we hope to demonstrate that a positively charged fog is efficient in contacting and wetting the 1 micron respirable particles that are hard to remove by other techniques. If this work is successful it will be a major contribution to the improvement of industrial health in the United States. A paper on this topic was given at the 1974 Miami meeting of the AIGH. A copy of the paper is attached in the appendix.

We have made an effort to predict the effect that electrostatic phenomena might have in keeping dust in suspension. A simplified mathematical treatment based on the book by Allis and Herlin⁶ is attached to this report as an appendix. The results suggest that even on earth electrostatic effects might be a significant factor in dust suspension. This dust suspension phenomena is associated with the normally negative electric charge of the earth. There have been a number of observations of a positively charged layer of particles near ground level, with a negatively charged layer at a higher altitude⁷. The work of Israel, cited as reference 7, was a source of this type of information. In particular, he notes (pg. 453) that haze layers associated with temperature inversions were negatively charged. Mist and fog seemed to become more negatively charged as the amount of humidity in the air increased (pg. 455-6).

Other studies by Criswell^{8, 9} have been focused on the levitation of dust grains on the moon because of charging by solar photons. The dust is quite visible in the photographs returned by Surveyor 7. Criswell suggests that dust grains as large as 6 microns in diameter are levitated 30 cm above the lunar surface. We are exchanging data with Dr. Criswell and if he feels the information is needed we may undertake a short term study of the charge acquired by various materials exposed to a simulated solar photon flux.

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9. Criswell, D. R., "Horizon-Glow and the Motion of Lunar Dust," *Photon and Particle Interactions with Surfaces in Space*, pg. 545-556, D. Reidel Publishing Co., Holland, Ed. by R. J. L. Gard.

C. Other Activities in the Laboratory

The ARPA/Air Force sponsored studies on the relationship between fatigue and subsequent exoelectron emission have been finished. We have demonstrated an exoelectron system for scanning along an aircraft structure to detect cracks or crack growth during flight. This technique has been extended to the monitoring of stress-relief annealing processes. The first results of these studies have been published (publication 17), and later results have appeared, May 1973 (publication 19).

The exoelectron-fatigue studies will be continuing with the support of the Naval Air Development Center. The major topic of interest will be the carbon composites that are being used for aircraft construction.

The silicosis aspects of the dust program have been discussed in an earlier section. We anticipate that this work will continue with the support of an industrial organization. Another activity, supported by the City of Tucson and internal University funds involves the generation of methane (natural gas) from garbage and sewage. Some use was made of NASA owned equipment in this work and a copy of our report to the City is attached. This paper was given at the El Paso Composting Conference in May 1974 and it appears that the City will fund a larger pilot plant study of the process. This is another example of the overlap between the Space Program and research of benefit to the general public.

It is most important to note that the programs discussed above were supported by a number of agencies, including NASA, the Air Force, NSF, and the University of Arizona. The exchange of funds and equipment

provided by the various programs has been of significant aid in many facets of this research. In all of these efforts the funding from the NASA grant has allowed us to support important programs during the intervals between other research grants. Without this long-term assistance many of our studies would never have been started.

Another use of Laboratory facilities occurs in connection with two courses taught by Professor Hoenig in Electronics and Instrumentation for graduate students in the Zoological, Geological, and Medical Sciences. These students use the Laboratory and its apparatus for demonstrations and simple projects. Again, this would be impossible without the long-term support we have received from NASA.

IV. PERSONNEL

Students who have been supported by the grant and their present activities are listed below:

1. Donald Collins, M. S., 1963; Ph.D., California Institute of Technology, September 1969. Research Associate, California Institute of Technology.
2. George Rozgoni, Ph.D., 1963; Senior Staff Member, Bell Telephone Laboratories, Murray Hill, New Jersey.
3. Donald Creighton, Ph.D., 1964; Professor, University of Missouri, Rolla. (Partial NASA support.)
4. Col. C. W. Carlson M. S., 1965; Active duty, U. S. Army.
5. Melvin Eisenstadt, Ph.D., 1965; Professor of Mechanical Engineering, University of Puerto Rico, Mayaguez, P. R.
6. John Lane, M. S., 1968; Philco Ford Company, Tucson.
7. William Ott, M. S., 1970; Burr-Brown Research, Tucson. (Partial NASA support.)
8. Richard Pope, M. S., 1970; Hewlett-Packard Corporation, Palo Alto, California.
9. Robert Goetz, M. S., 1972; Ph.D. Candidate, Biomedical Engineering, University of Arizona.
10. Freedoon Tamjidi, M. S., 1972; Westinghouse Company, Phoenix, Arizona.

V. PUBLICATIONS CENERATED TO DATE BY RESEARCH ON THIS GRANT

S. A. Hoenig and Others

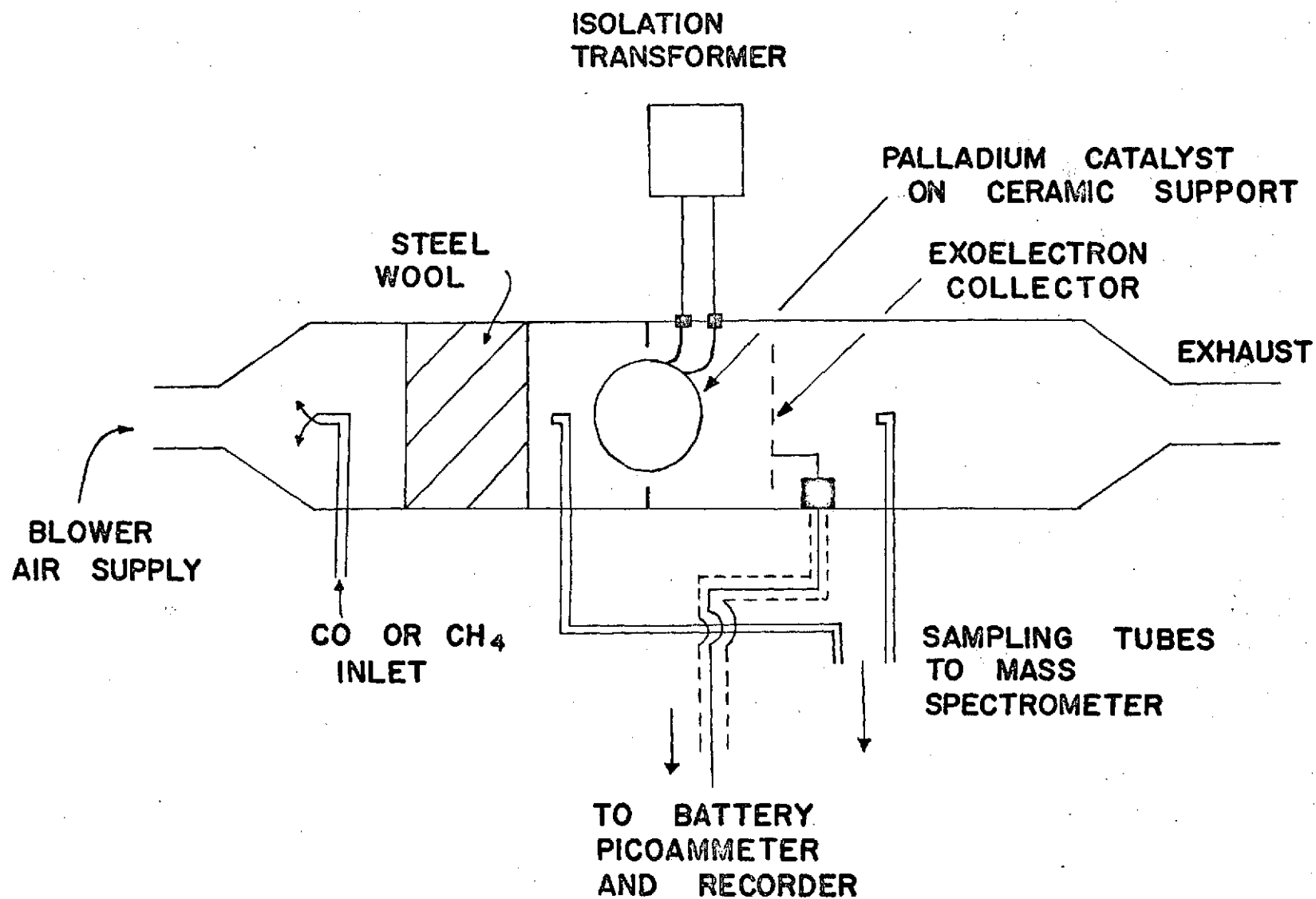
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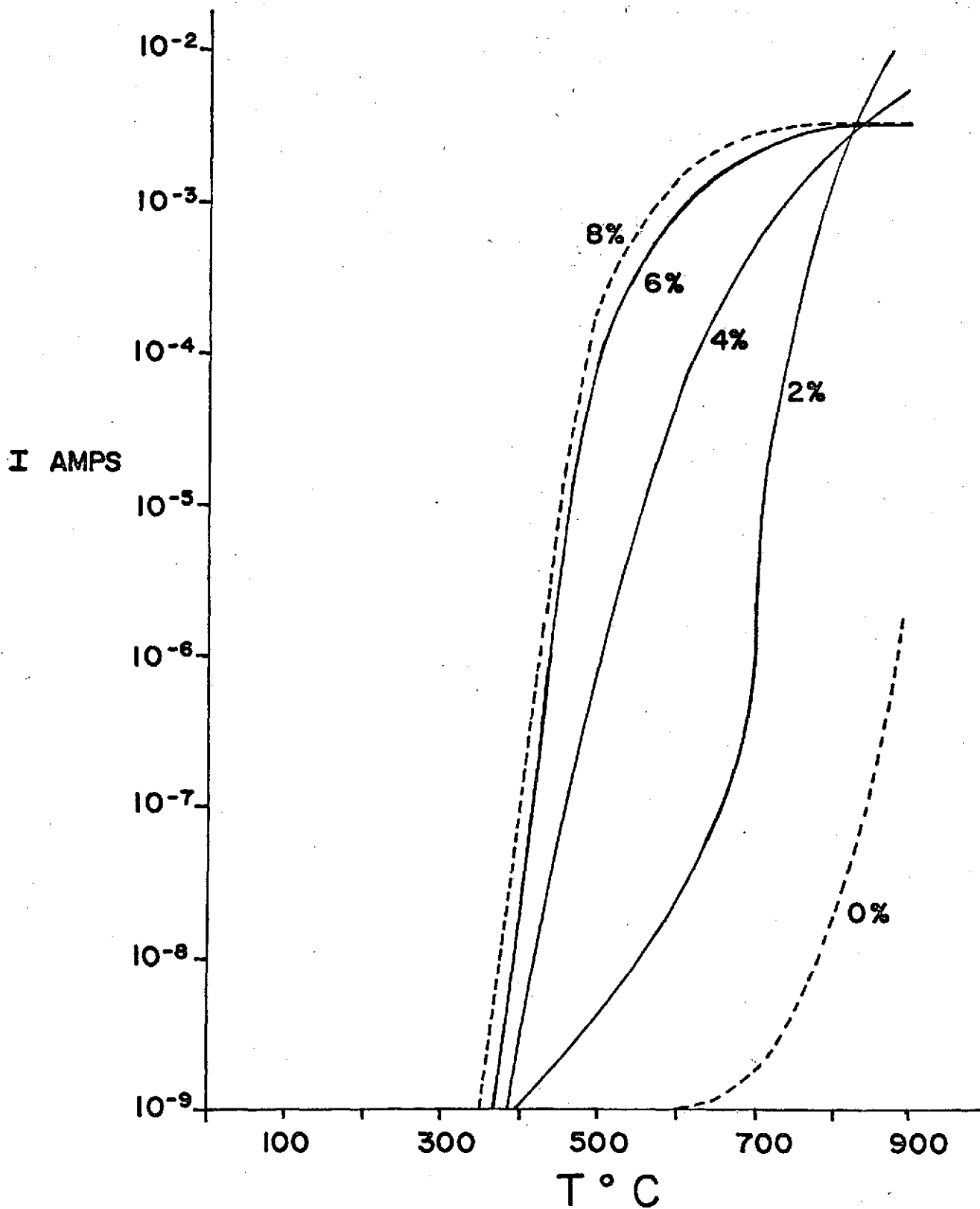
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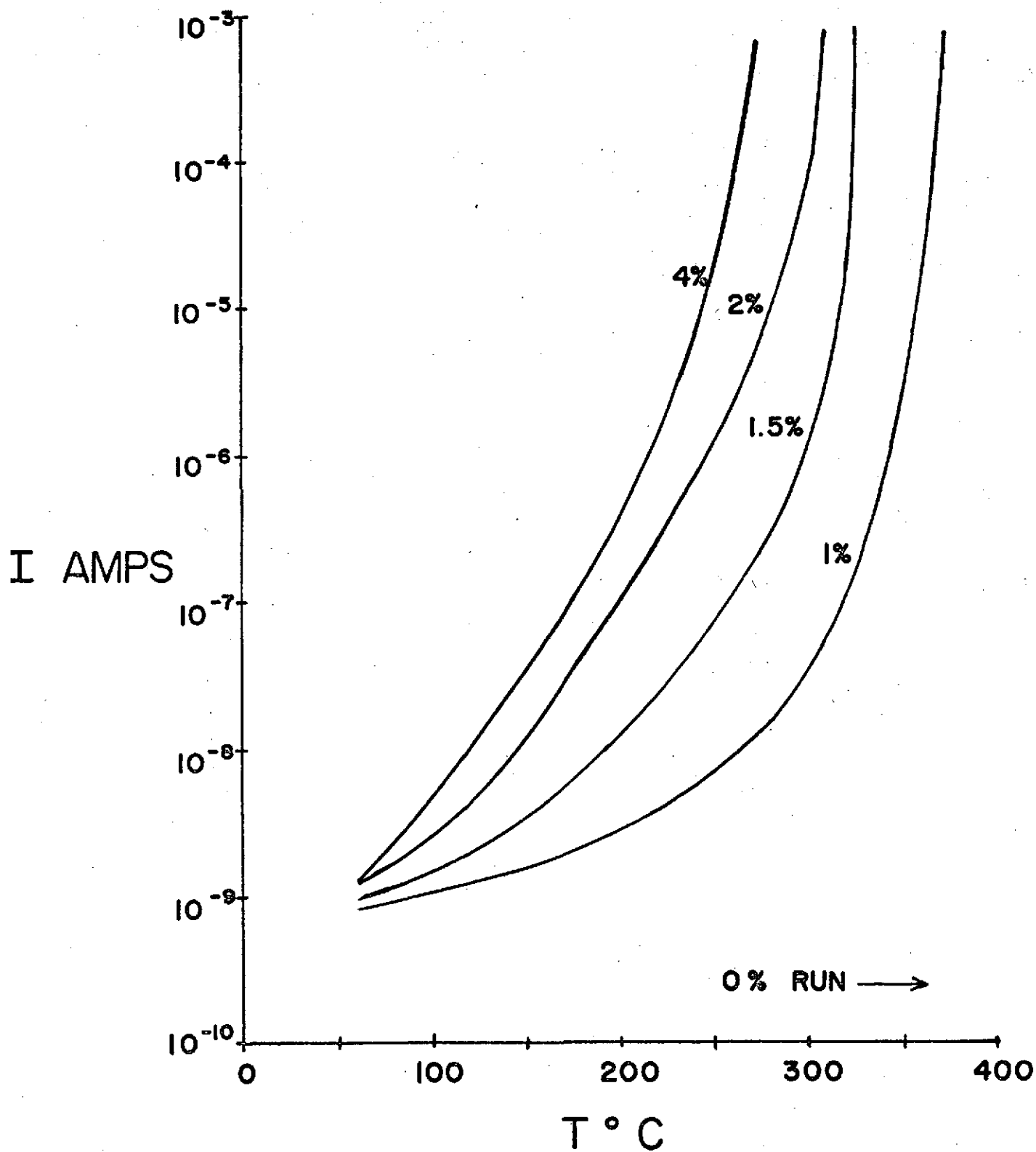
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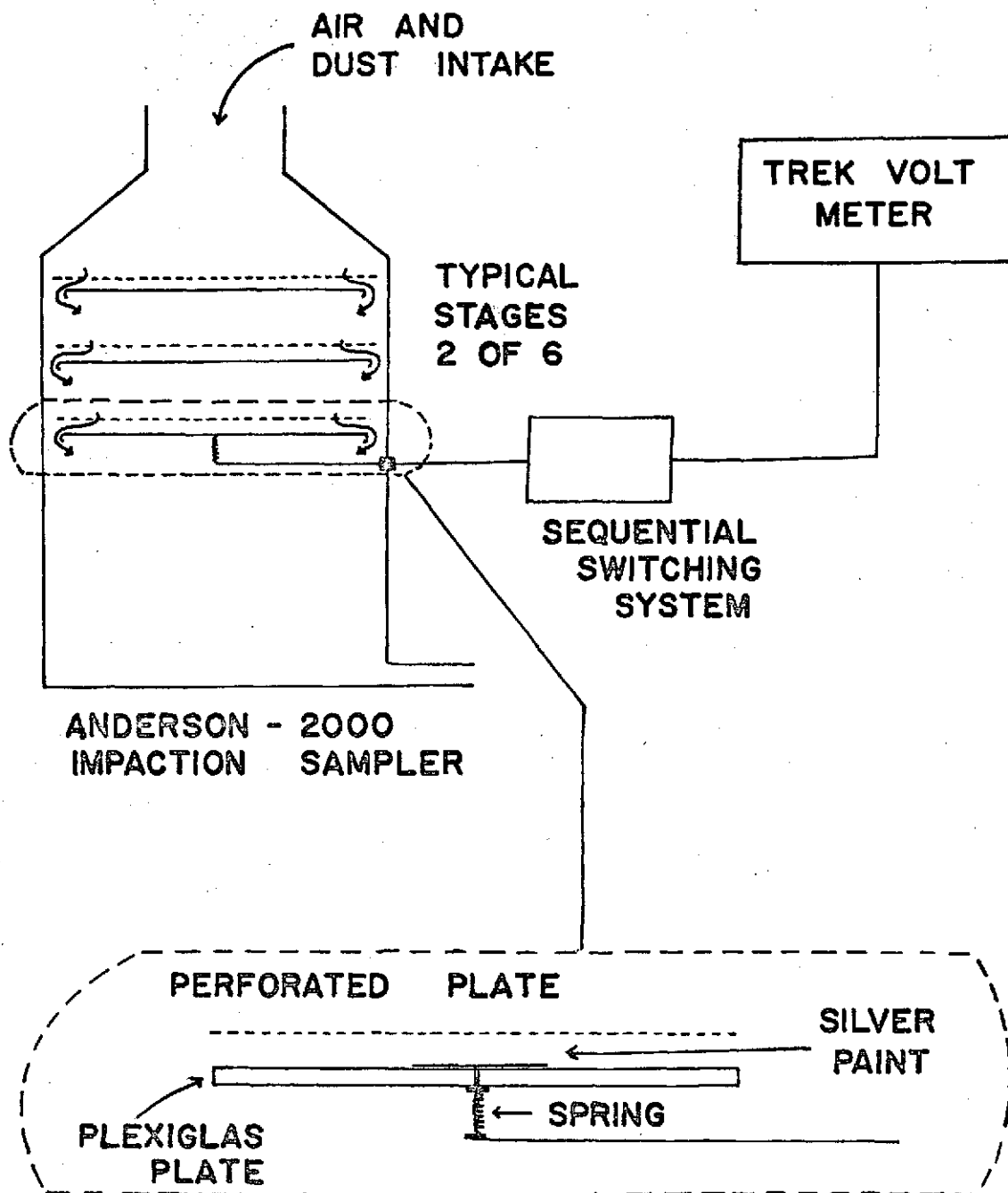


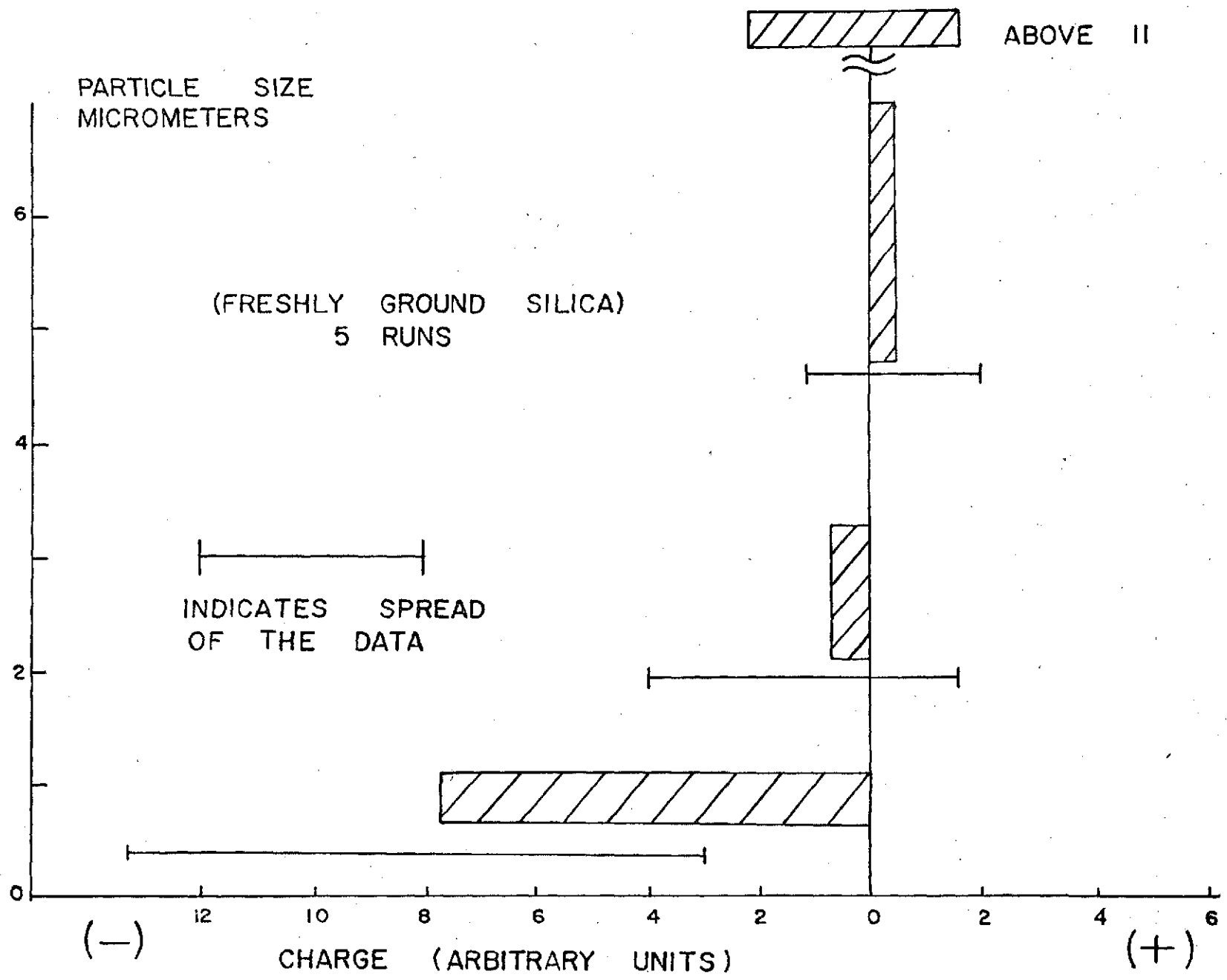


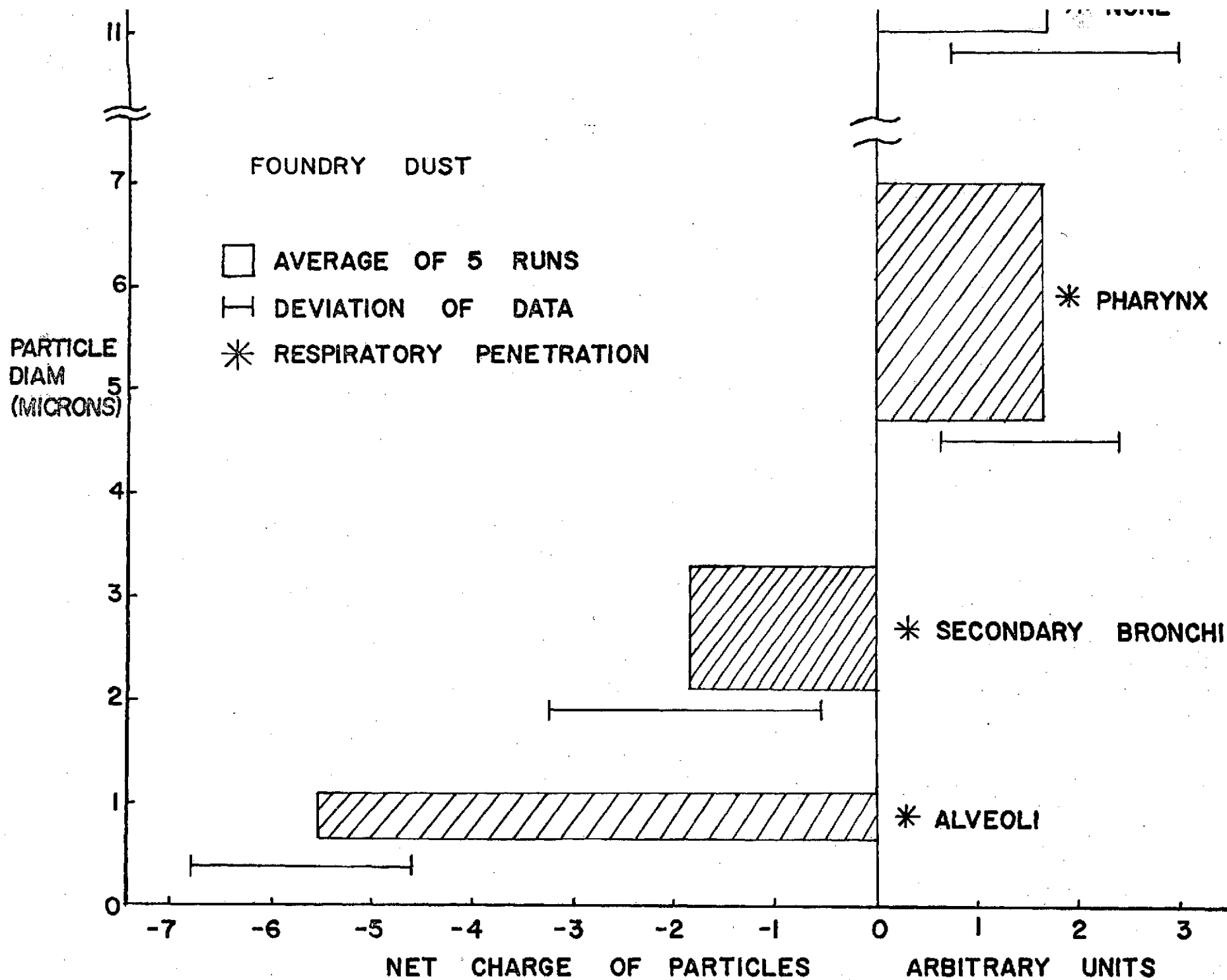
EXOELECTRON CURRENT VS TEMPERATURE
AND CO PERCENTAGE IN AIR



EXOELECTRON CURRENT VS TEMPERATURE
AND PERCENT CH_4 IN AIR



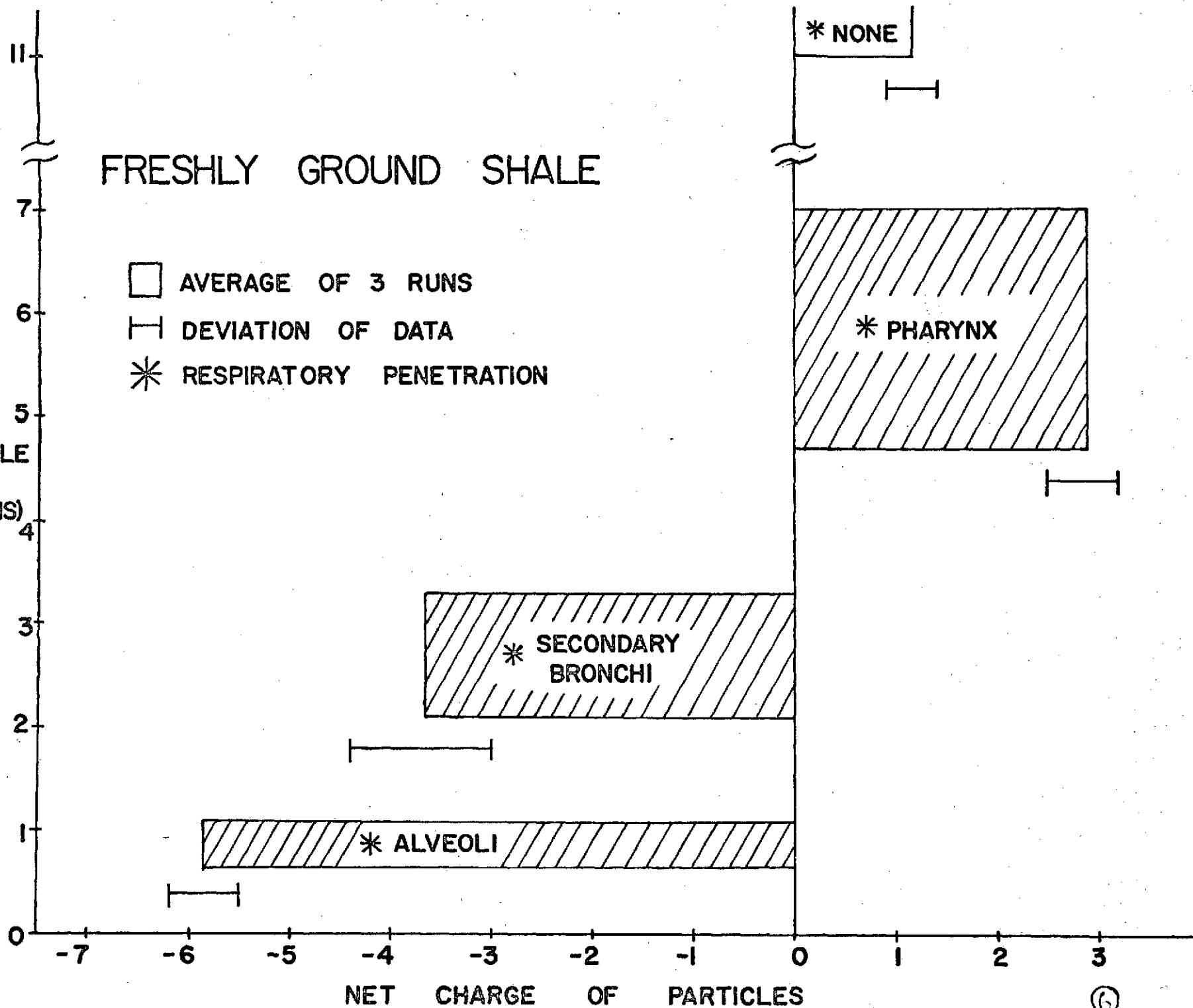


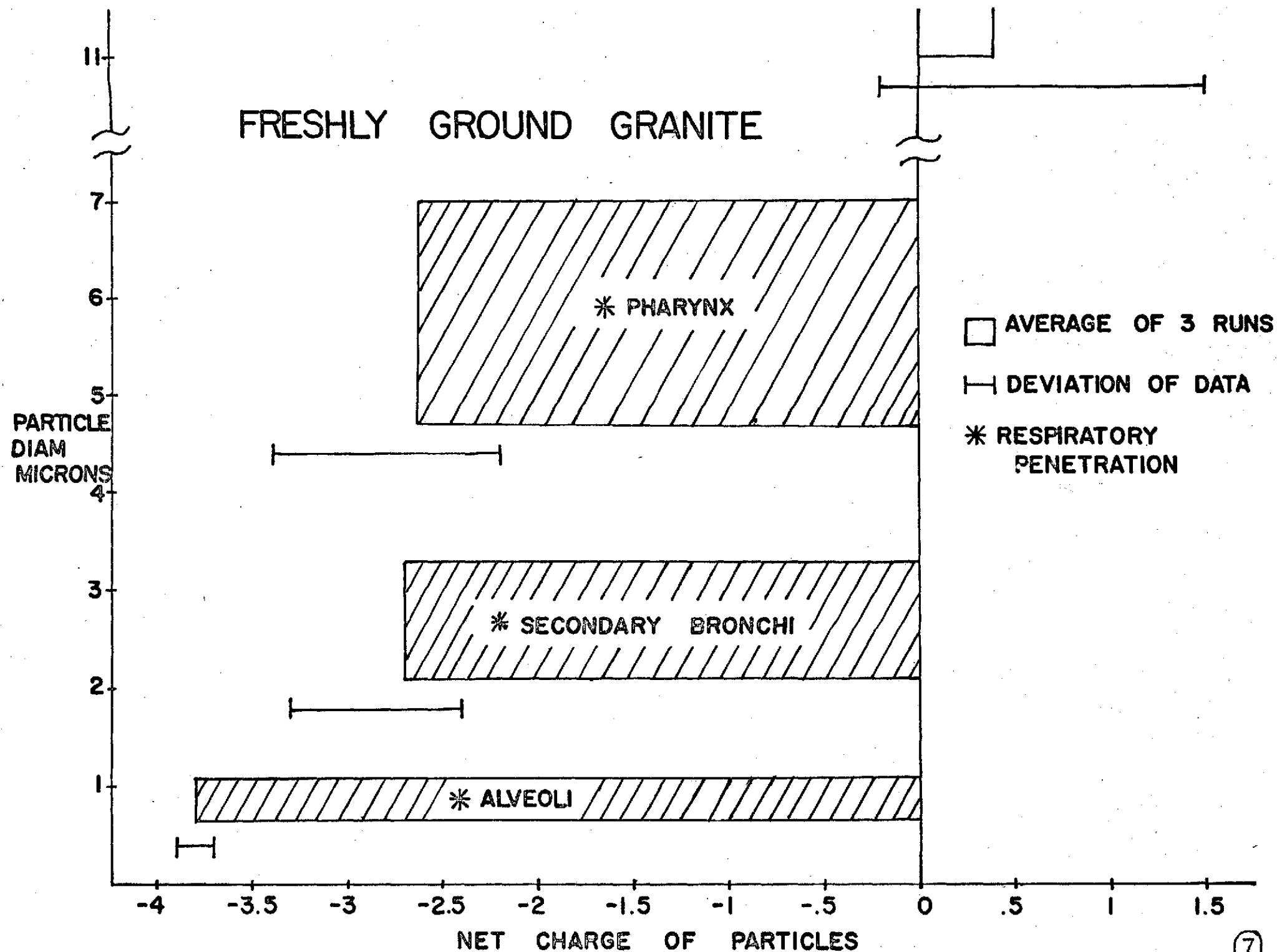


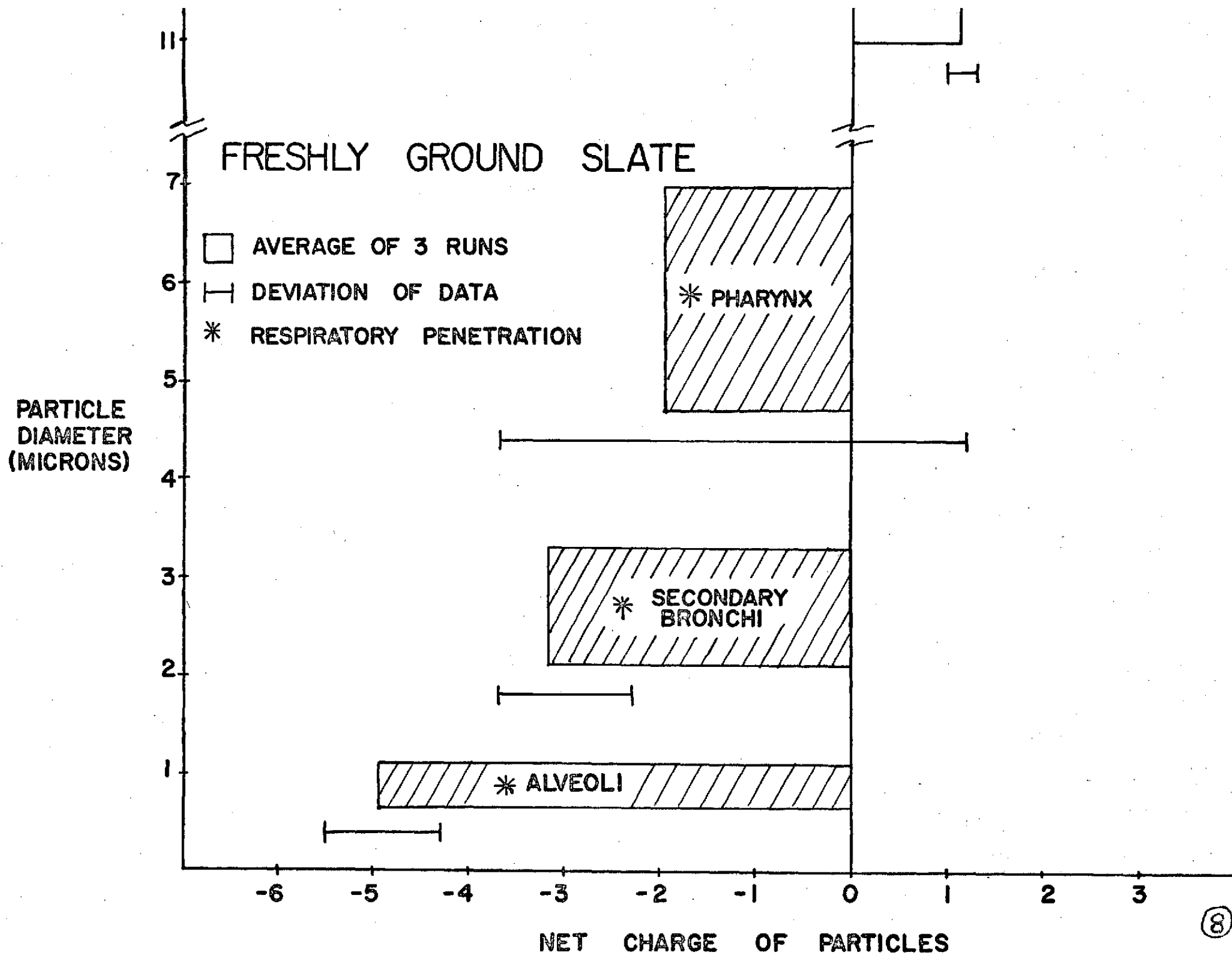
FRESHLY GROUND SHALE

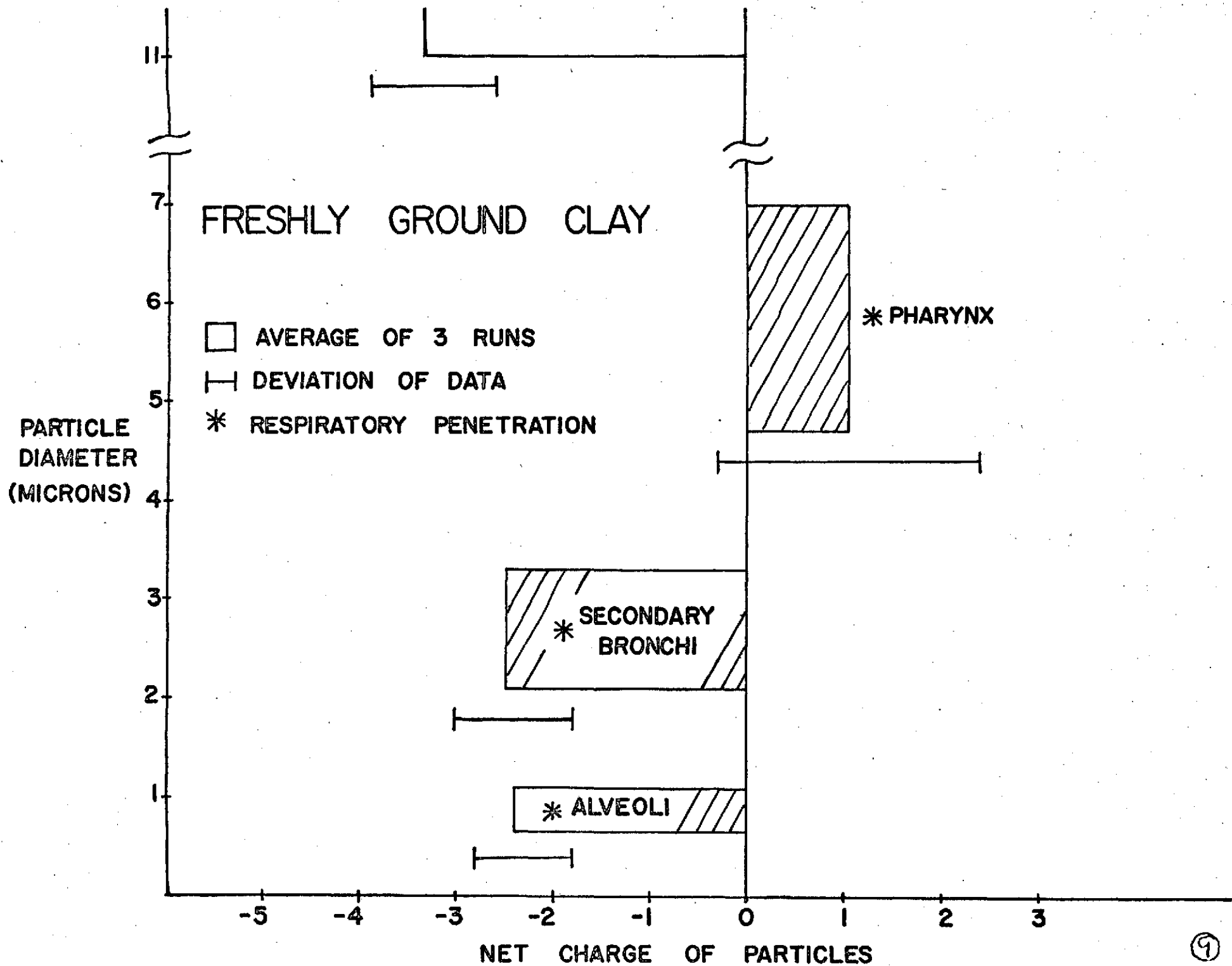
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- ┌─┐ DEVIATION OF DATA
- * RESPIRATORY PENETRATION

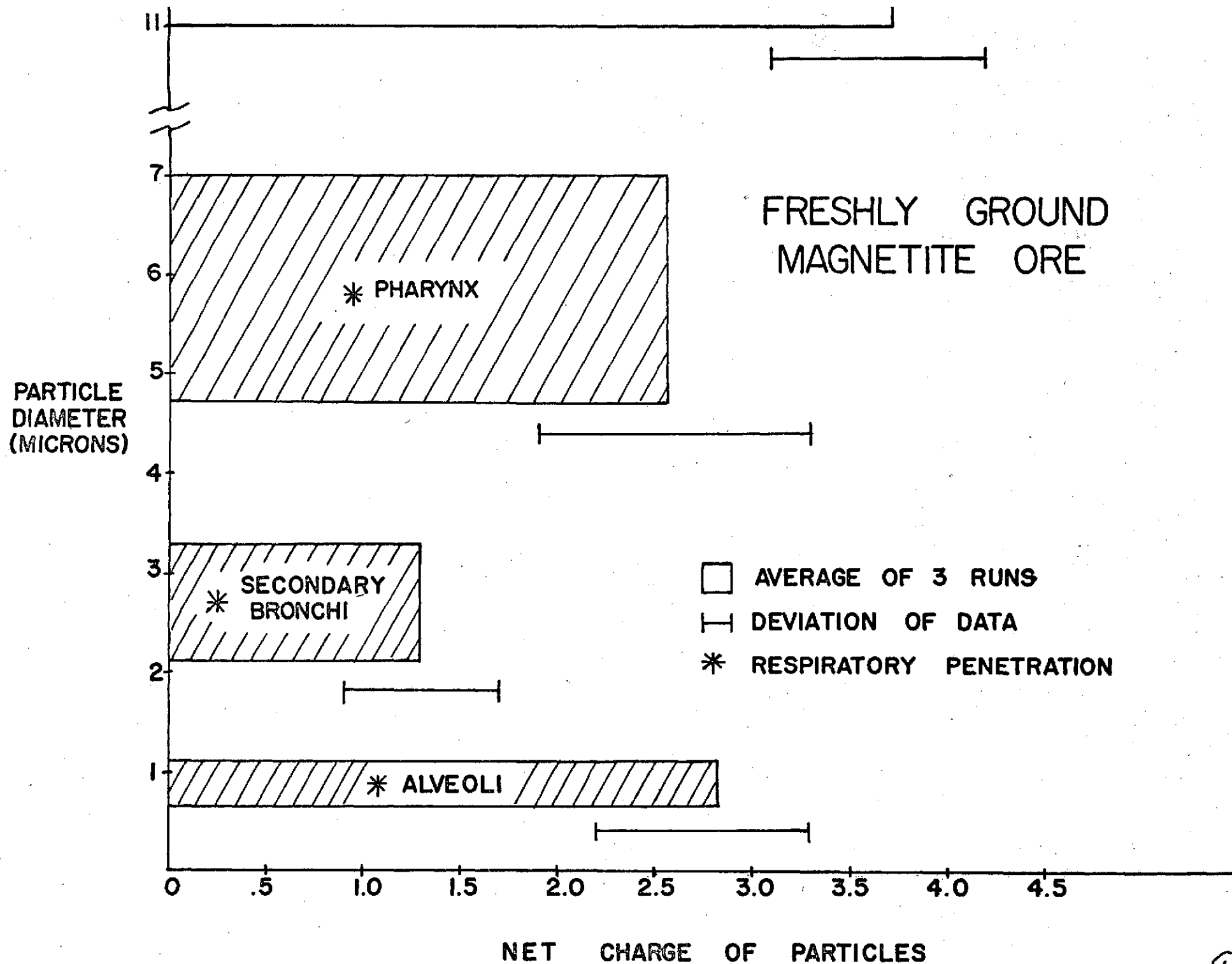
PARTICLE
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(MICRONS)

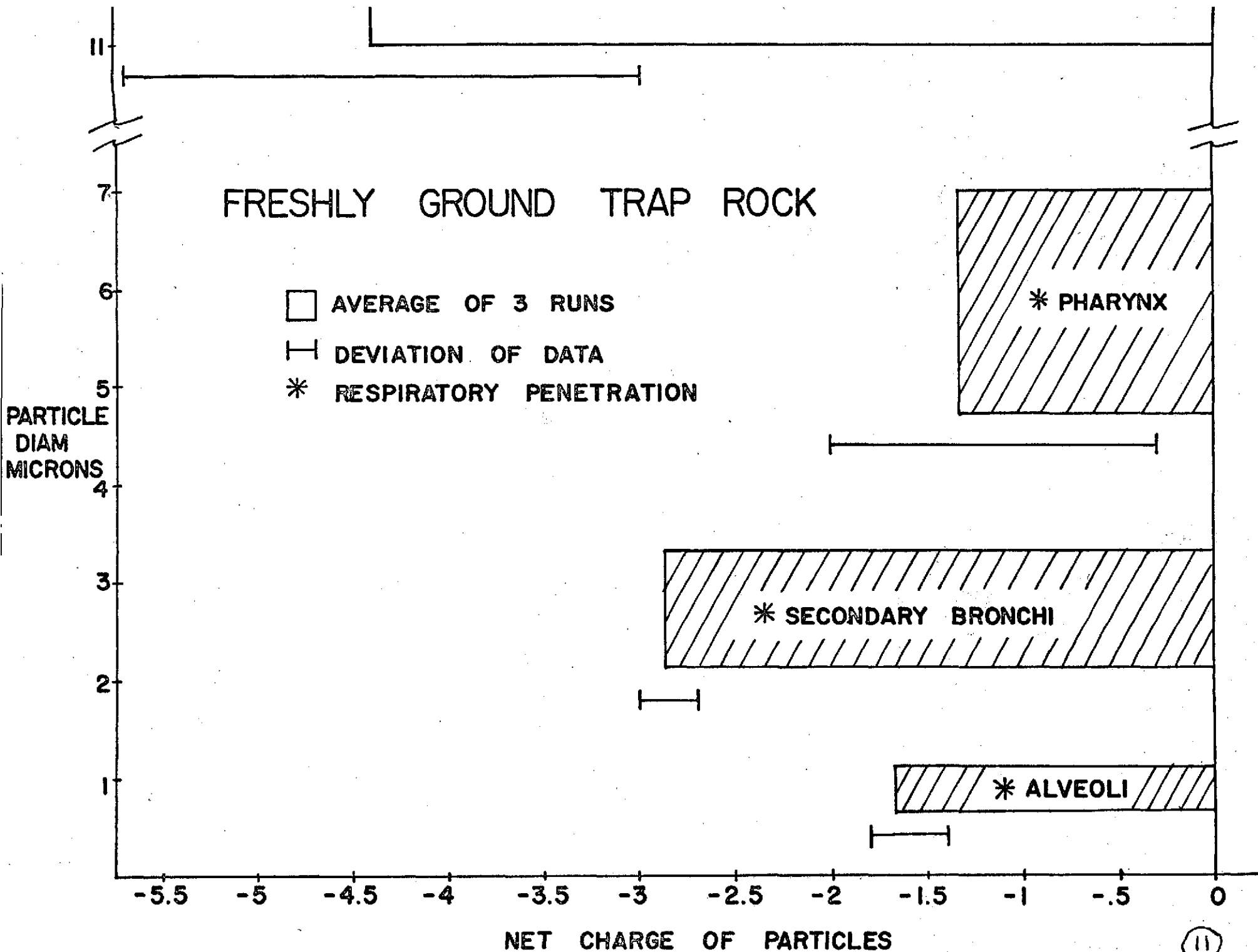


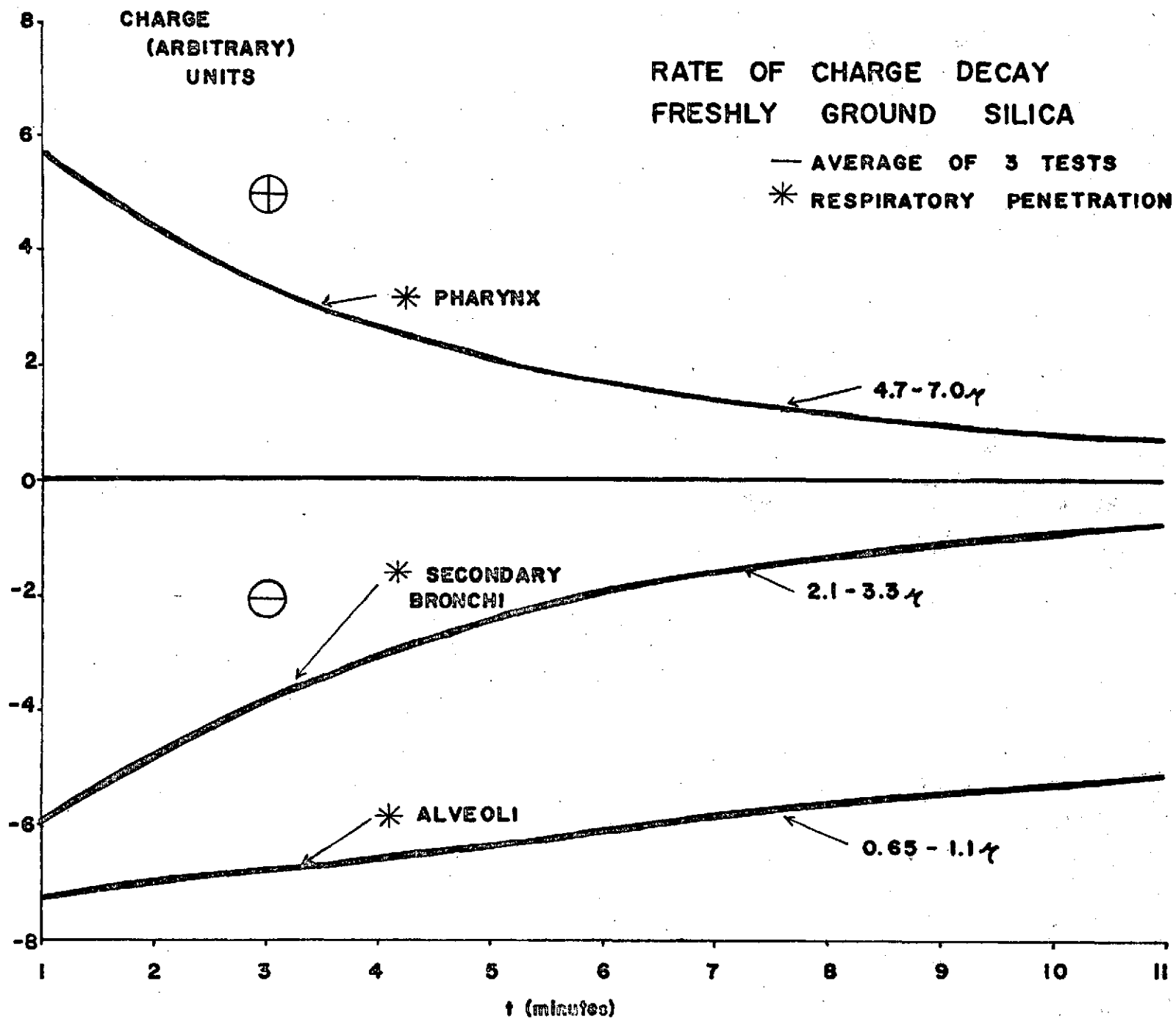


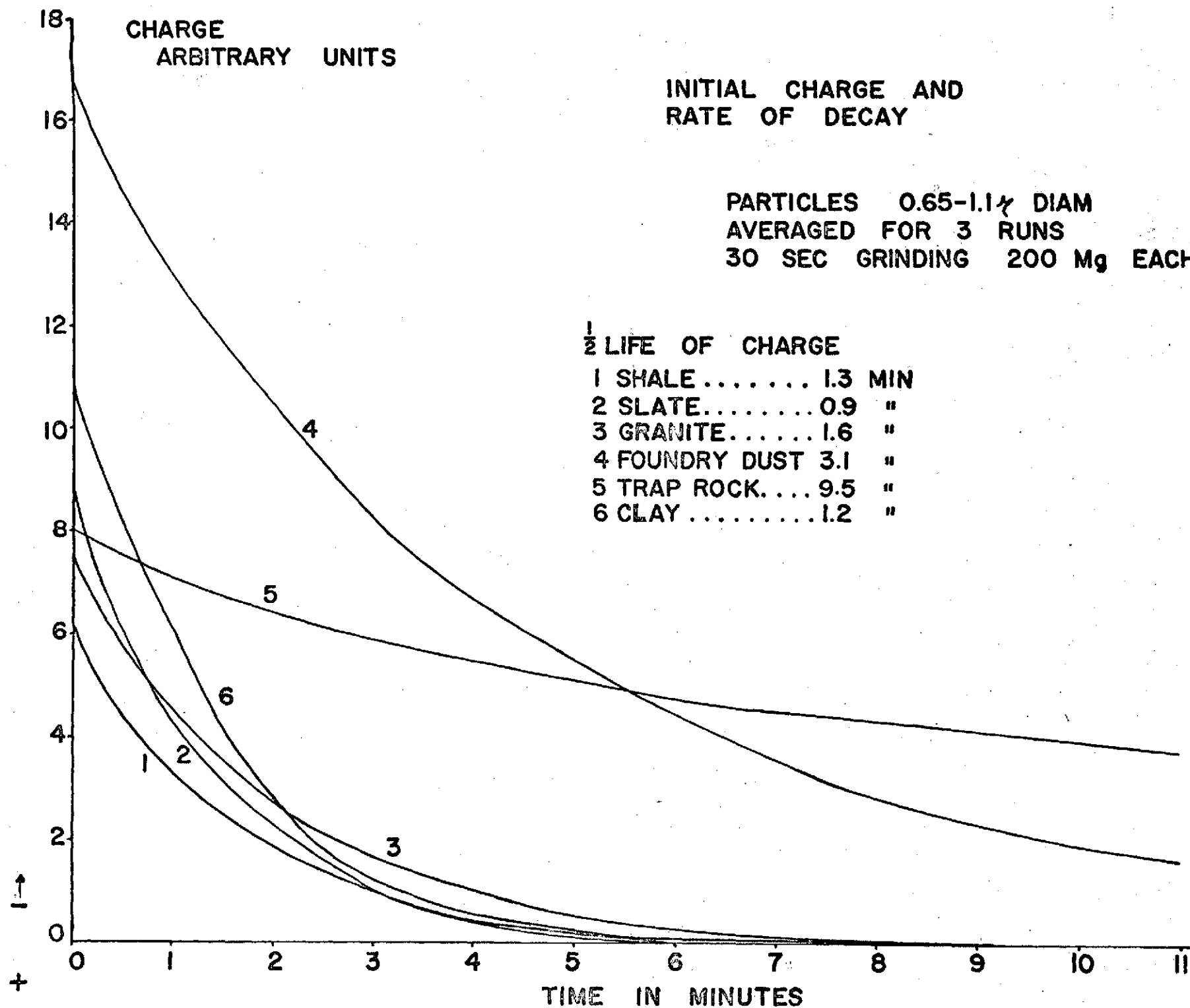










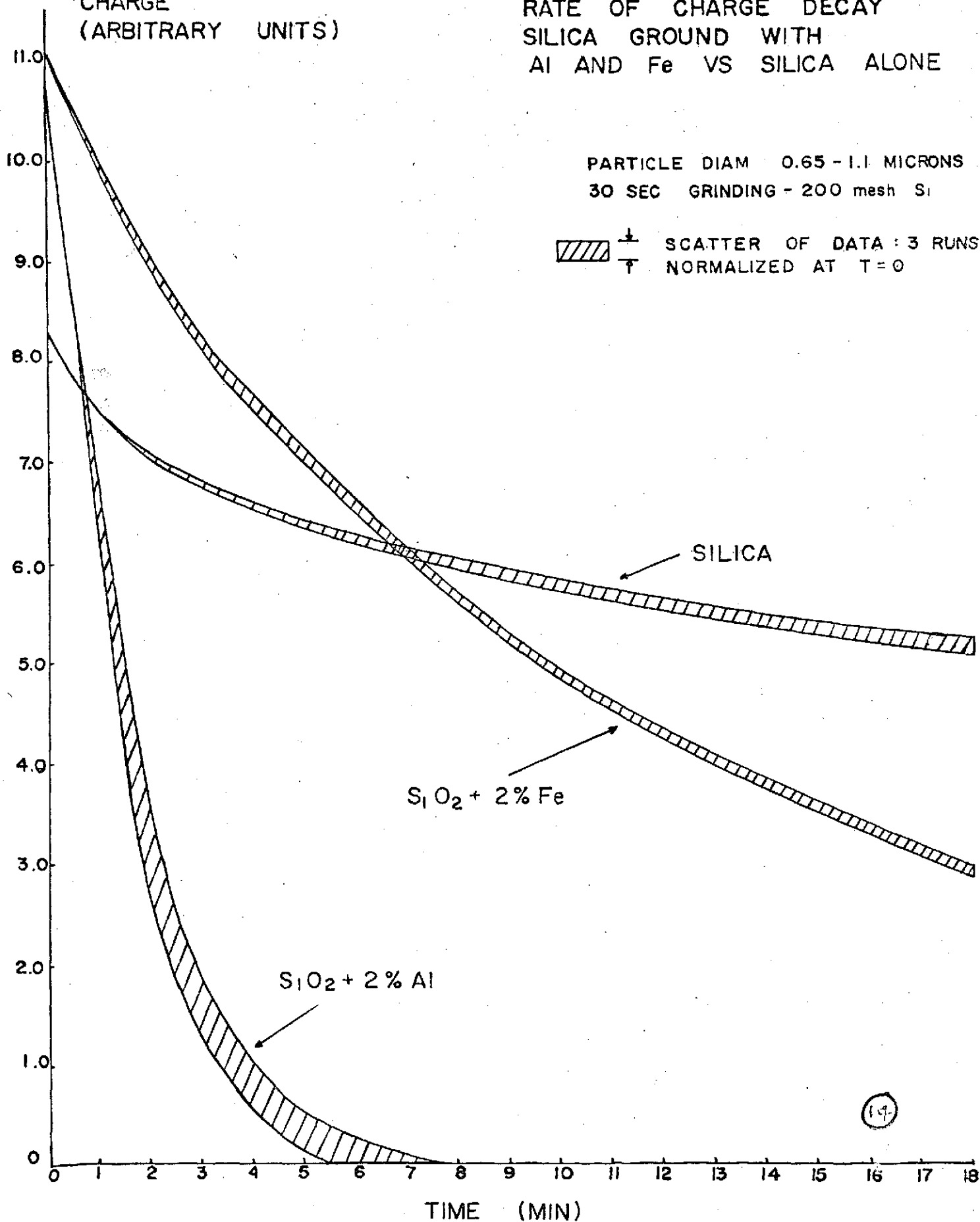


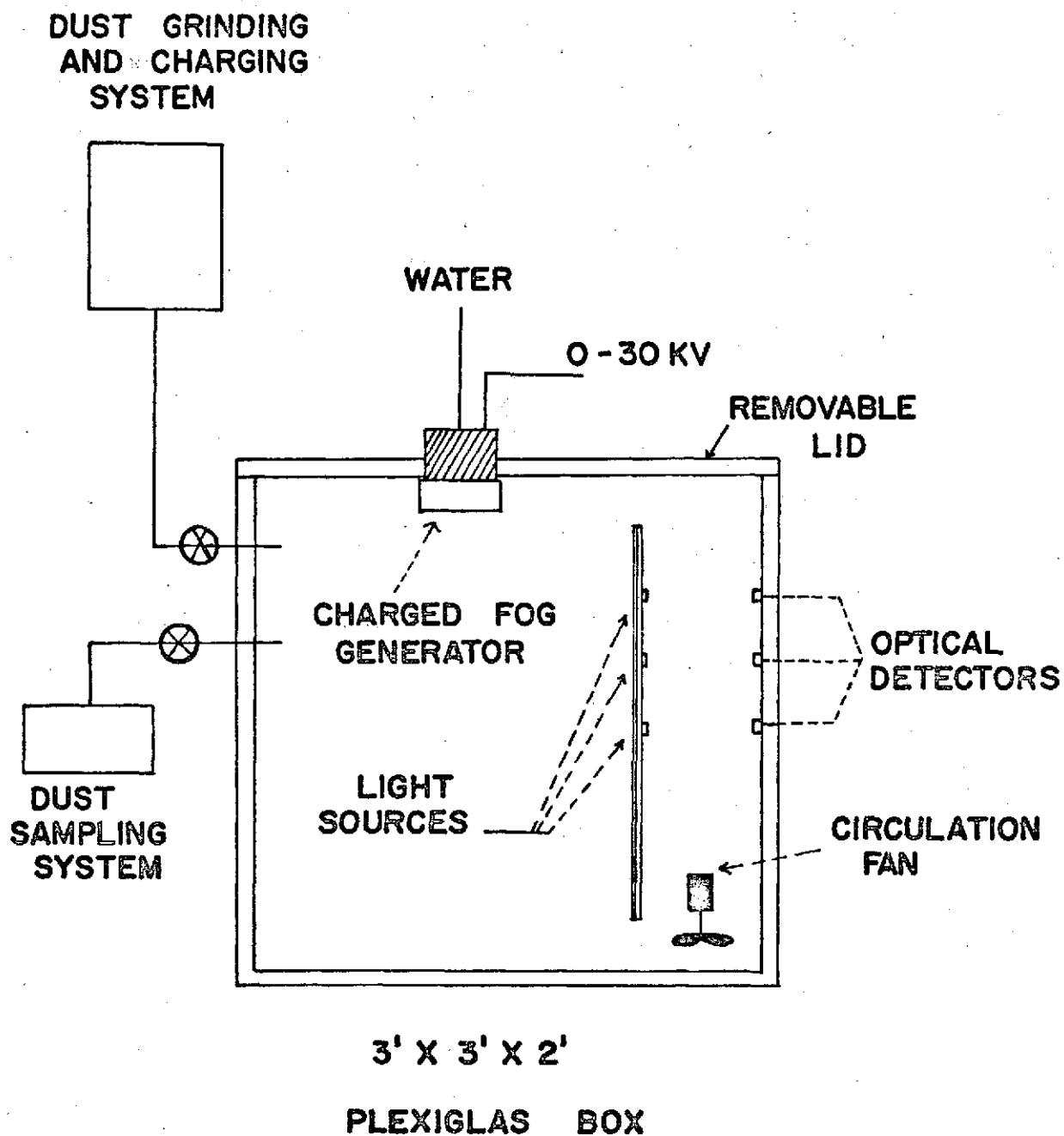
CHARGE
(ARBITRARY UNITS)

RATE OF CHARGE DECAY
SILICA GROUND WITH
Al AND Fe VS SILICA ALONE

PARTICLE DIAM 0.65 - 1.1 MICRONS
30 SEC GRINDING - 200 mesh Si

 \pm SCATTER OF DATA : 3 RUNS
 \uparrow NORMALIZED AT T = 0





APPENDICES

1. Exoelectron Emission from Freshly Ground Silica Materials and the Induction of Silicosis.
2. Analysis of Electrostatic Levitation Effects.
3. A System for Methane Recovery and Fertilizer Production from Garbage and Sewage.

APPENDIX 1

EXOELECTRON EMISSION FROM FRESHLY GROUND SILICA MATERIALS AND THE INDUCTION OF SILICOSIS

EXOELECTRON EMISSION FROM FRESHLY
GROUND SILICA MINERALS

and

THE INDUCTION OF SILICOSIS

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*Presented at the May 15, 1974 Meeting of the American
Industrial Hygiene Association, Miami, Florida*

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and the National Science Foundation is gratefully acknowledged.

ABSTRACT

We have investigated the electrostatic charge on freshly ground industrial minerals as a function of particle size. It appears that with most materials the one micron, respirable fraction, is negatively charged and we suggest that the charge might be exploited for control of this dust.

In a parallel study we have examined the mechanism by which silica particles interact with lung tissue. The details of this process including the potentiating and prophylactic effects of iron and aluminum have been elucidated.

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I. DUST GRINDING STUDIES

In last years paper [1] we reported on experimental studies of exoelectron emission (EEE) after grinding silica materials. At that time the grinding and dust collection system involved a modified ball mill and a vacuum pump to pull-off a sample of dust that was then deposited on a grounded metal screen. The exoelectron emission from the dust was measured as a function of time for various silica, iron, aluminum mixtures. We reported that the overall charge of the dust sample appeared to be negative and that iron enhanced the electron emission while aluminum reduced it. At that time we had no way of separating the dust by size and it was suggested that the emission-charging effects, that we observed, might be due to the larger non-respirable dust fraction and had no application to the problem of human silicosis.

In the past year we have modified an Anderson 2000* impact sampler to allow us to measure the electrostatic charge of the dust fractions collected at various levels in the sampler. Measurement of charge offers several advantages over the observation of exoelectron emission, first is the high input impedance of the charge measuring system which limits the decay of the dust charge. A pile of dust has a very low electrical conductivity and if EEE occurs from one layer of dust the charge of that

*The cooperation of the Anderson 2000 Company of Atlanta, Georgia in helping us obtain this unit is gratefully acknowledged.

layer will be lost. The low conductivity of the dust prevents recharging from the dust layers below the surface.

Another advantage of the charge measurement system is its ability to detect positively charged as well as negatively charged dust, this was not possible with the EEE system since it used a collector at + 90 volts above ground. The dust analyzer and associated electronics are shown in Figure 1, the charge analyzer was manufactured by the Trek Company of Gasport, New York, their cooperation in helping us to adapt their equipment to our needs is gratefully acknowledged.

A typical experiment involved grinding a sample with a clean mortar and pestle and then pulling it into the Anderson sampler with a small vacuum pump (the flow through the sampler was held at the value suggested by the manufacturer). When the entire sample had been picked up, the pump was stopped and the measurement began. The automatic sequencer switched the charge measurement system from one level of the sampler to another. The charge at each stage was monitored by the Trek unit and a chart recorder. The switching system made use of magnetically driven reed switches operating in a make-before-break sequence to avoid any surge that might drive the Trek system off scale, (the details of the sequential electrical switching system will be published in the Review of Scientific Instruments).

Typical results of a number of measurements of this type are shown in Figure 2, the material here was silica sand and it is interesting to note that the 1 micron, respirable dust is negatively charged.

The larger fractions tend to be either positively charged or neutral. Other data of this type on foundry dust, supplied by Mr. John Crable of NIOSH, Cincinnati, is shown in Figure 3, we see again that the respirable dust is negatively charged and the effect is somewhat larger than that observed with silica alone. Similar results on shale are shown in Figure 4.

Other data showing the decay of the negative charge on the 1 micron sized silica dust is shown in Figure 5. It is interesting to note that the rate-of-decay of the 1 micron sized material is rather slow indicating that this dust will still be charged when it reaches the alveoli.

More data on charge decay versus time for several industrial materials is shown in Figure 6. Here we used "school samples" supplied by Mr. John Crable and it is interesting to note that the foundry dust, which we would expect to be contaminated with iron has the largest negative charge and a rather slow rate of decay with time. This is in agreement with the results reported at last years meeting in Boston [1].

Other data showing the effect of added iron and aluminum on the charge and decay of freshly ground, 1 micron, silica is given in Figure 7. Iron produces a higher charge and aluminum a lower charge, again in agreement with the results reported last year. This "aluminum effect" may be connected with the "well known" properties of aluminum for prophylaxis of silicosis [2,3,4].

Other data of this type, on a variety of samples, is being obtained but the slides were not ready in time for the present meeting. In general we observe that the 1 micron fraction is negatively charged and the implications of this are worth consideration. If the respirable fraction, that presents a hazard to the human lungs, is negatively charged it might be possible to selectively remove that fraction quite efficiently by means of a positively charged water fog. The studies of reference [5 and 6] indicate that charged fog is significantly more effective than uncharged fog in contacting respirable sized dust particles.

The effect here is two fold; first of course are the electrostatic effects. A charged 1 micron dust particle and an oppositely charged water droplet of the same size will be attracted to one another by electrostatic effects. This vastly increases the possibility that the water drop will wet the particle and begin the agglomeration process that can bring the particle to the ground. A second advantage of the charged fog system, over conventional water sprinkling, is the smaller use of water and the slow fall-out of fog droplets. Coarse water sprays are ineffective in removing 1 micron dust because the rapidly falling drops actually sweep 1 micron dust particles *out of their path* rather than capturing them by collision.

Another aspect of data on negatively charged 1 micron particles is the possibility that they could be levitated or at least delayed in falling out by the negative electrostatic field of the earth itself [7]. If dust-cloud layers are to some extent supported by levitation [7], the

addition of a positively charged fog would help bring the dust particles down. This technique for dust removal will be investigated in the next year of study.

II. THE MECHANISM OF SILICOSIS

In last years paper [1] we discussed some preliminary data on the use of red blood cells (RBC) as a measure of the pathogenicity of silica dust. This work has been extended and we have begun to unravel the details of how silica interacts with RBC membrane. The details will be published in Environmental Research but the results can be summarized here.

A silica particle enters the alveoli and is immediately rendered inert by a coating of protein material picked up from the lung. The coated silica particle is recognized as a foreign body by the lung defense system and a macrophage (modified white blood cell) engulfs the particle so that it can be removed through the mucosal or lymph system.

After the coated silica particle has been engulfed by the macrophage a reaction between the lysosome (inside the macrophage) and the particle destroys the lysosomal membrane. The contents of the lysosomal sac attack the protein coating of the silica particle and the macrophage membrane. The macrophage is destroyed and the silica particle is released into the lung tissue. The contents of the macrophage include a fibrogenic factor that produces the disease we call silicosis.

The phenomena is quantitative in the sense that a small quantity of silica is gradually removed from the body by a series of macrophages, each carrying the particle a short distance before it is destroyed. The fibrosis that is induced is widely diffused and does not interfere with breathing. If a great deal of silica is present there is intense local fibrosis, due to the large number of dead macrophages, and the silica is trapped in the familiar fibrotic nodules of silicosis.

The prophylactic effect of aluminum follows from the fact that it provides the silica particle with a coating that cannot be removed by the proteases in the lysosome. The particle is inert and the normal lung clearance mechanism removes it.

The next phase of this study will involve the use of lung-macrophage preparations to verify our results from the red cell studies. In these experiments we will add several physical and chemical modifications of silica to macrophage cultures. The amount of damage caused by the macrophage ingested silica will be determined by microscopic examination.

Another goal of this investigation is the development of a device for monitoring the hazard level of silica-containing dusts. The first series of experiments for this phase will involve measuring the strength of binding between different silica modifications and several well defined high molecular weight polymers (a polyanion, a polycation, and an uncharged polar polymer). This will be done by binding the polymers to various silica preparations and then measuring the release of polymer as

a function of pH, ionic concentration, and temperature. Subsequent experiments will be performed to correlate the polymer binding ability and macrophage damaging capacity of various silica modifications.

Our previous findings concerning the mechanism underlying the silica-membrane interaction leads us to predict that for one of the polymers tested there will be a consistent correlation between the *strength* of polymer binding and the *macrophage damaging properties* for each of the various silica preparations. If this proves to be true, then such a polymer will form the basis for our dust hazard monitoring device. This field-useable system would allow a dust sample to react with the proper polymer and precipitate a dye. The intensity of the color would be a direct measure of the hazard that the dust sample presents to the human lung. A test of this type would be more useful than the conventional silica analysis which takes no account of the type of silica or the presence of potentiating metals, i.e., iron or aluminum.

Our other goal in this project is the development of a sensitive and specific blood test for the early detection of silicotic injury. Our prediction that such a test is possible is based on our experimental results to date. We believe that when a silica particle is taken into the lysosomal organelle of the macrophage, the silica particle is divested of its coating of protein components by the various degradative enzymes of the lysosome. We suggest that these intracellular proteins will be denatured on the silica surface and will thereby present antigenic sites which are unique to silica-injured tissues. The uniqueness of these

antigenic sites derives from two factors: First, the proteins will be of intracellular origin; second, the proteins will be in a denatured configuration. We base this prediction of a denatured configuration on results presented by Schell [8] who has shown that when a protein is adsorbed onto the surface of silica, it gains new antigenic sites--presumably because it is in the denatured state.

The first question we will address ourselves to is: Are antibodies produced against silica particles? We will approach this problem by injecting charges of quartz dust, suspended in buffer, into the lungs of rabbits. A month or more will be allowed for development of the silicotic damage and any attendant antibody production.

At the end of this period a sample of rabbit blood will be taken and an antibody fraction prepared. If the antibodies are present in the blood of silicotic rabbits, our next step will be to determine if the antibodies are specific for the silica-protein complex, released from silica damaged membranes. If we can demonstrate that an antibody of this type exists it may be possible to develop a blood test for early, human, silicosis.

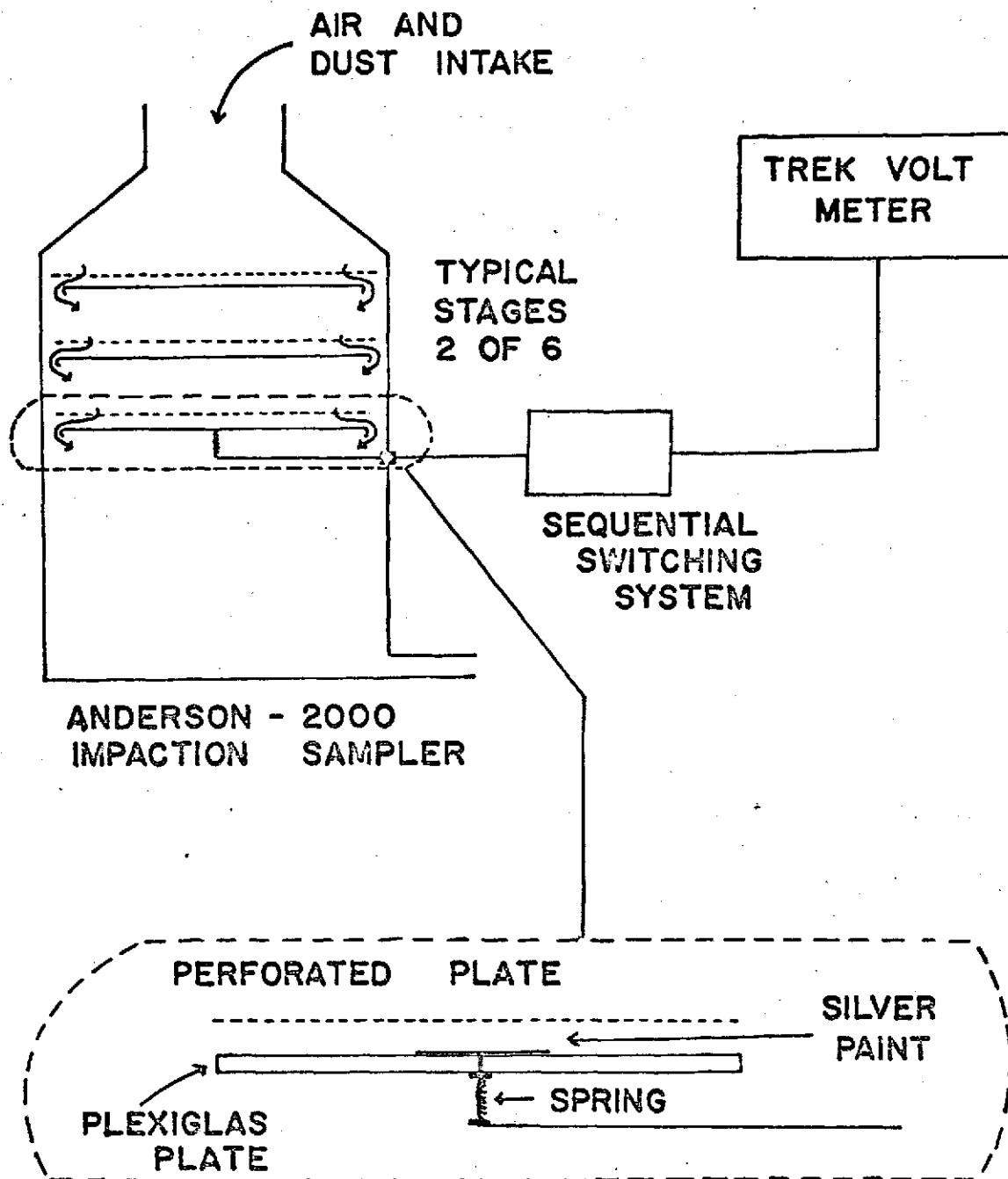
At present the detection of silicosis is often delayed until significant lung injury has developed. An early blood test would eliminate this hazard. A blood test would allow an employer to detect the onset of the disease in an individual, who may be highly sensitive to silica, before the damage from the disease is irreversable.

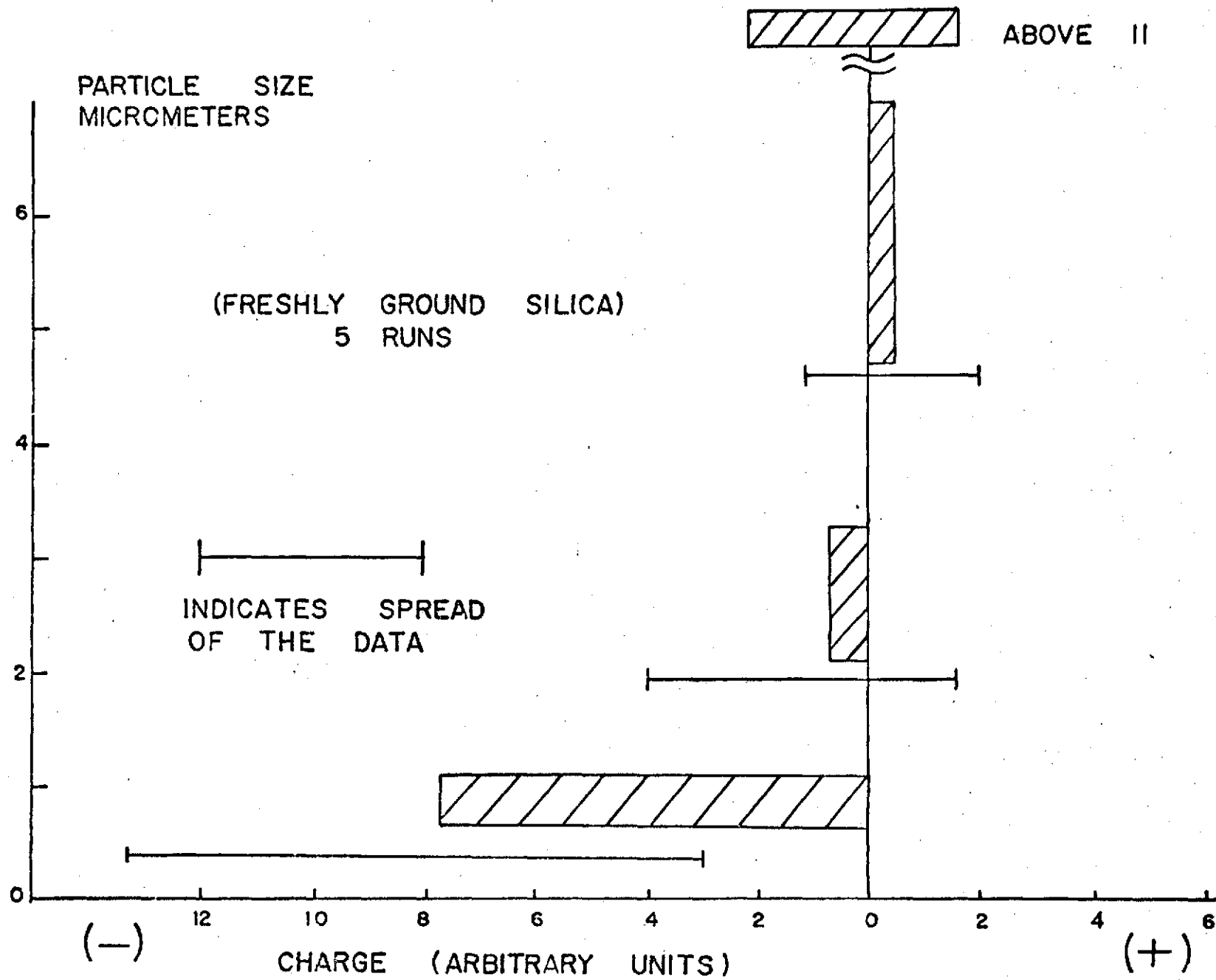
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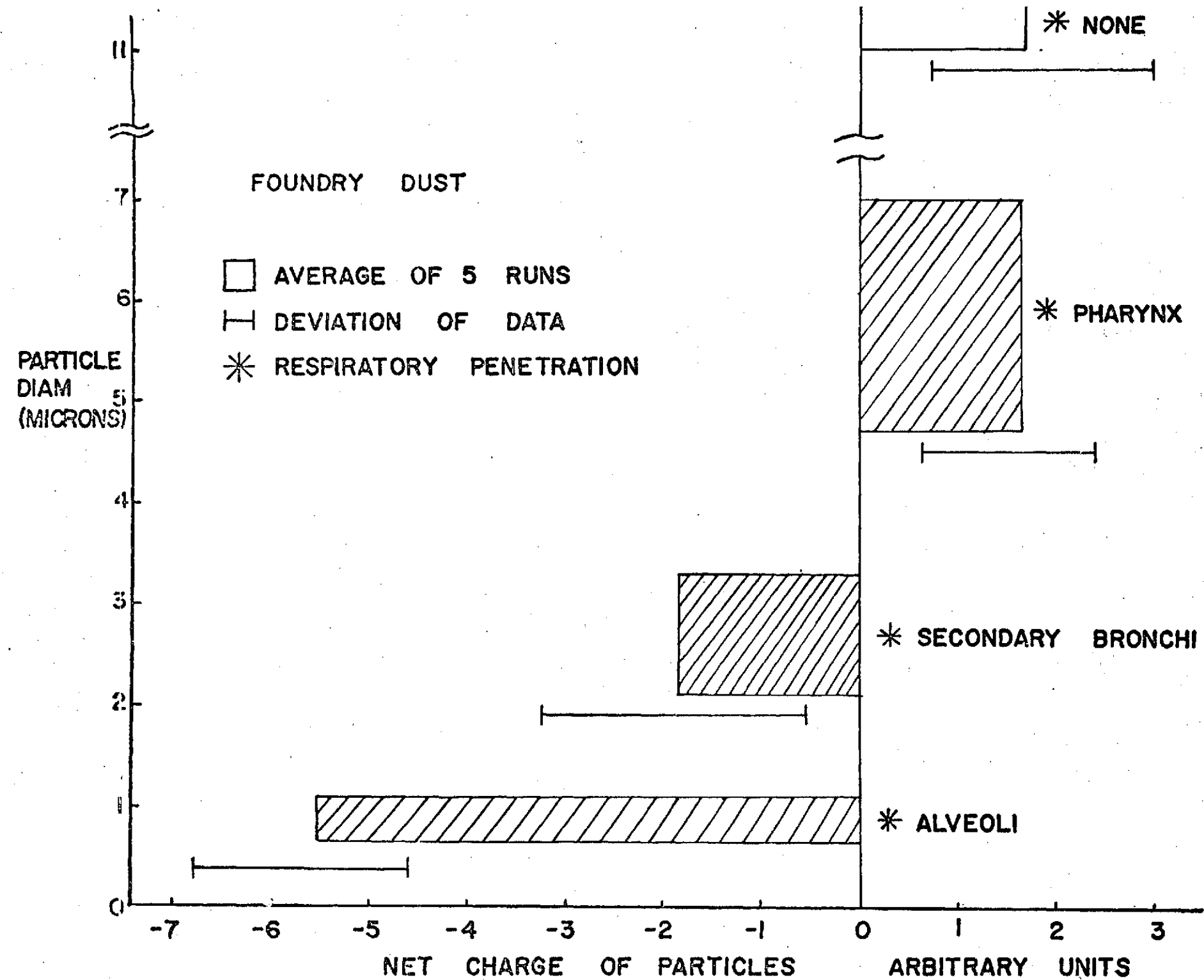
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LIST OF ILLUSTRATIONS

1. Impaction Sampler and Charge Measurement System.
2. Electrostatic Charge Versus Particle Size (Silica Sand).
3. Electrostatic Charge Versus Particle Size (Foundry Dust).
4. Electrostatic Charge Versus Particle Size (Shale).
5. Initial Charge and Rate of Decay (Silica Sand).
6. Initial Charge and Rate of Decay (Various Industrial Materials).
7. Initial Charge and Rate of Decay (Silica Sand with Added Iron or Aluminum).



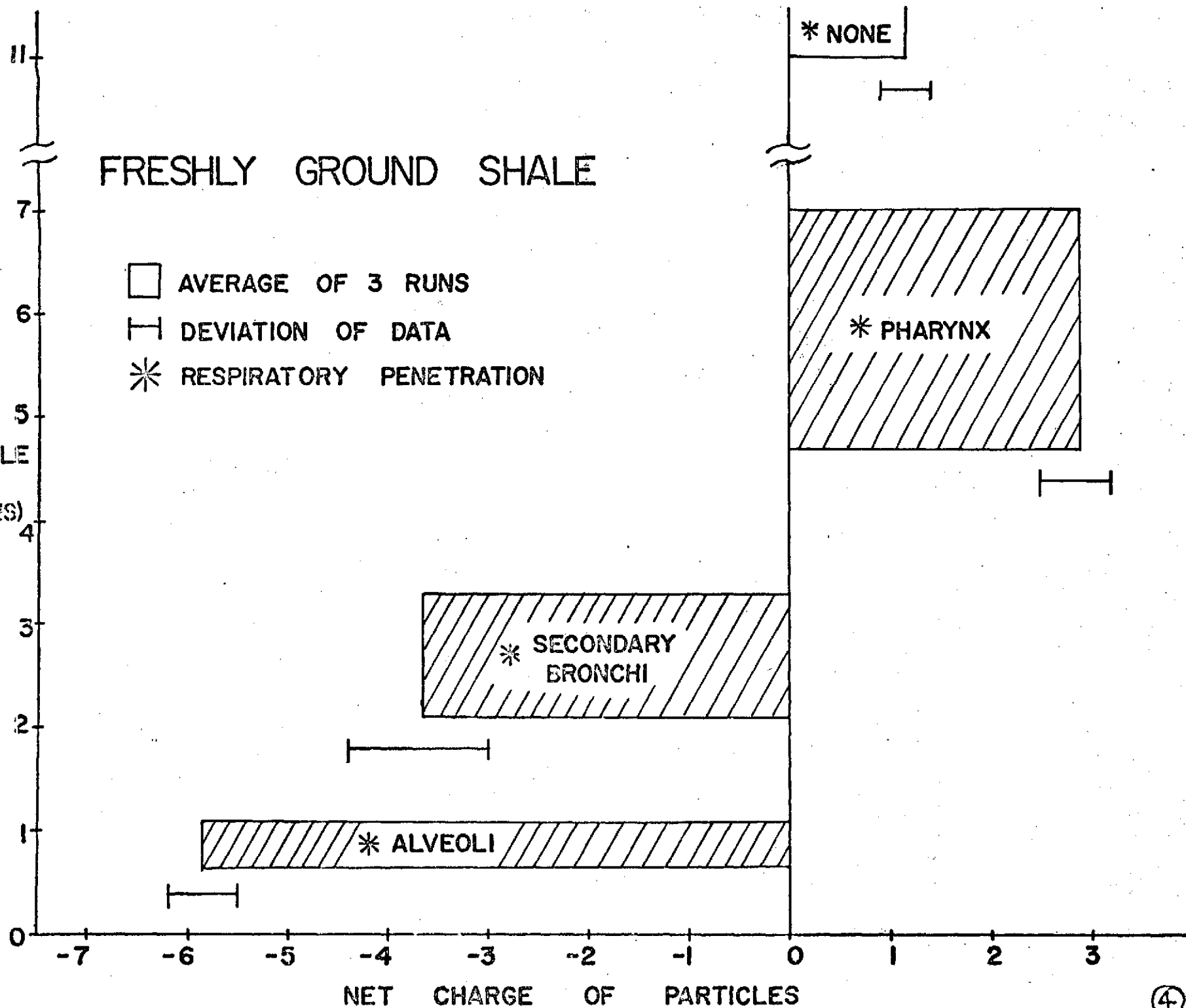


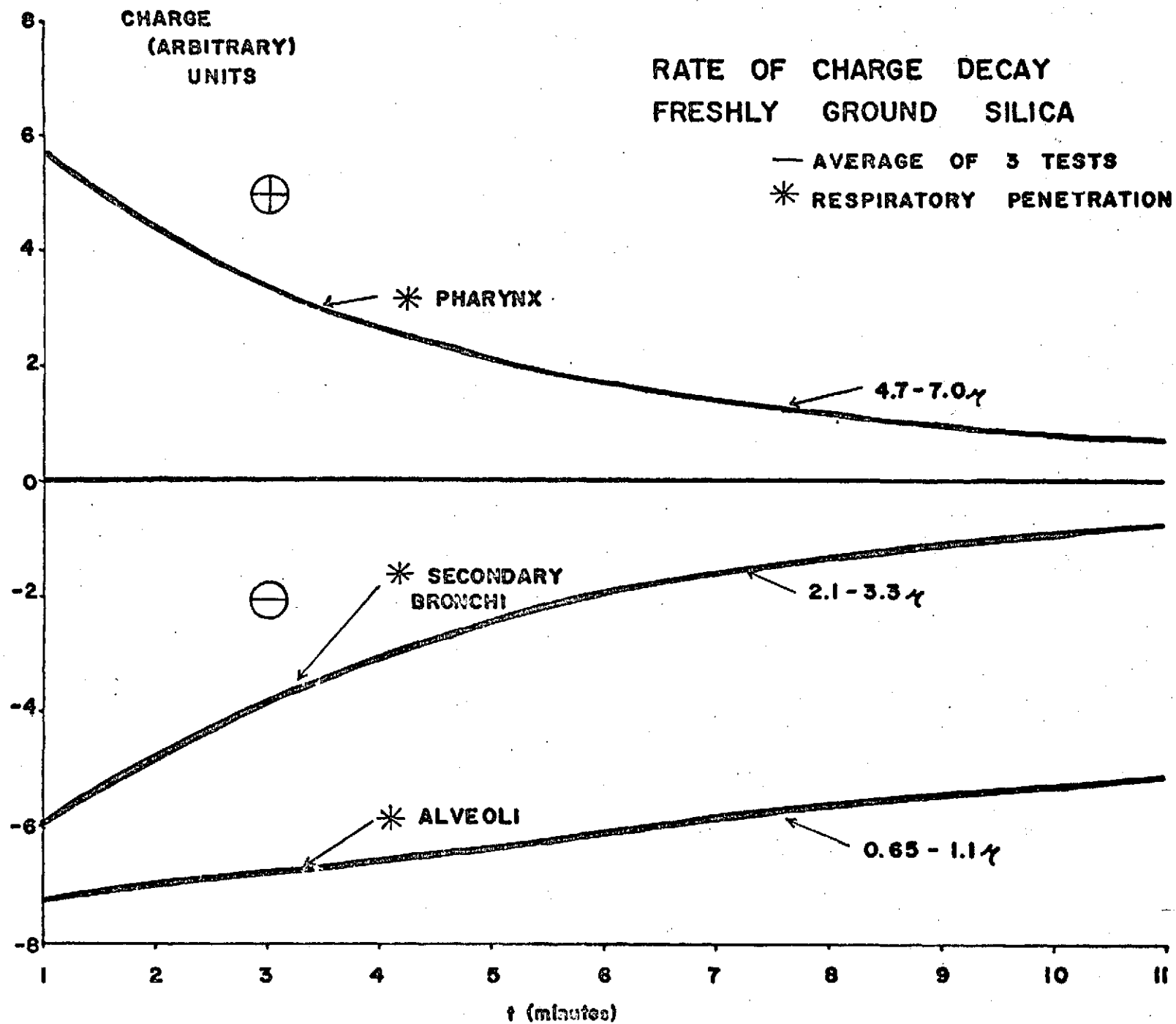


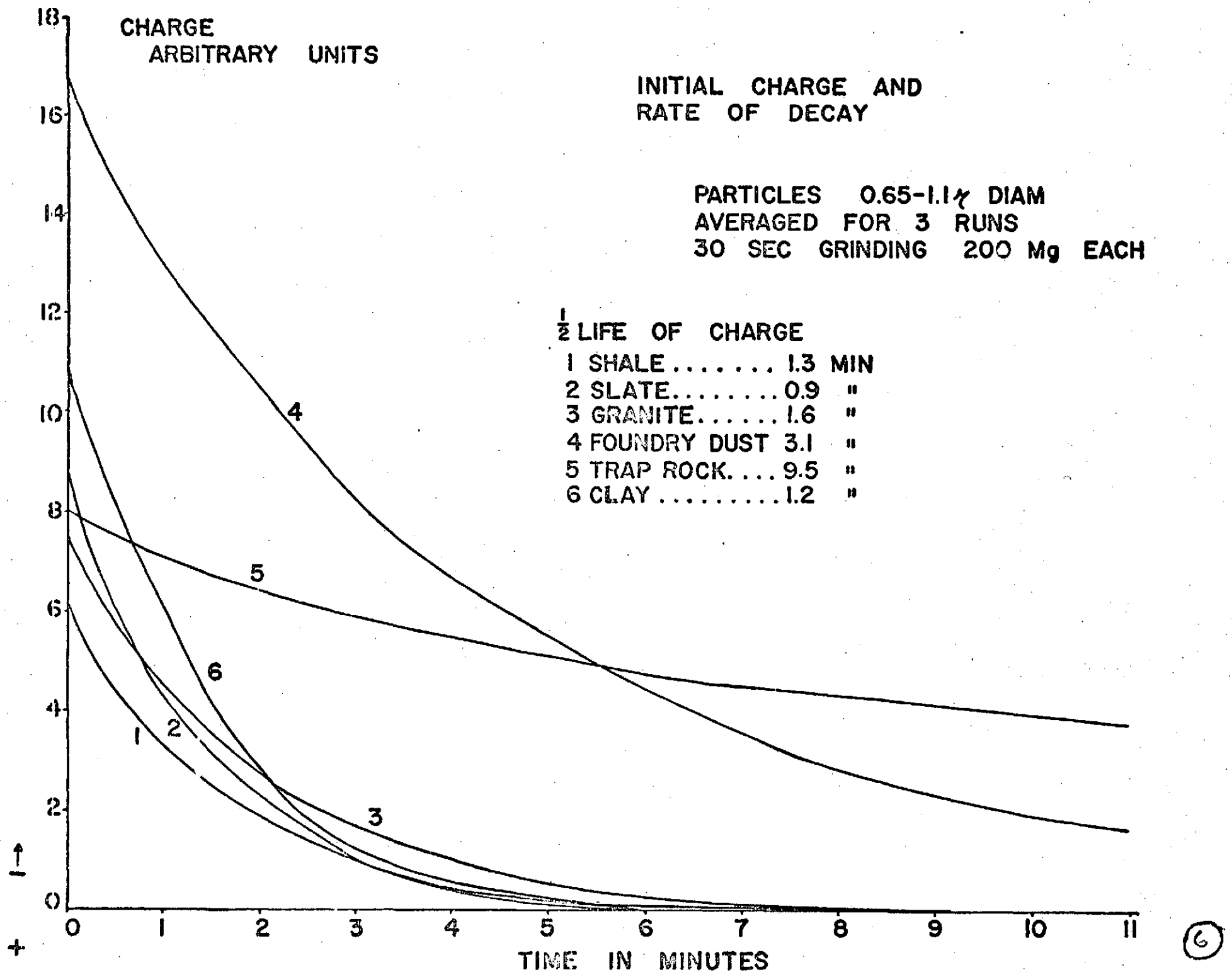
FRESHLY GROUND SHALE

- AVERAGE OF 3 RUNS
- ┌─┐ DEVIATION OF DATA
- * RESPIRATORY PENETRATION

PARTICLE
DIAM
(MICRONS)





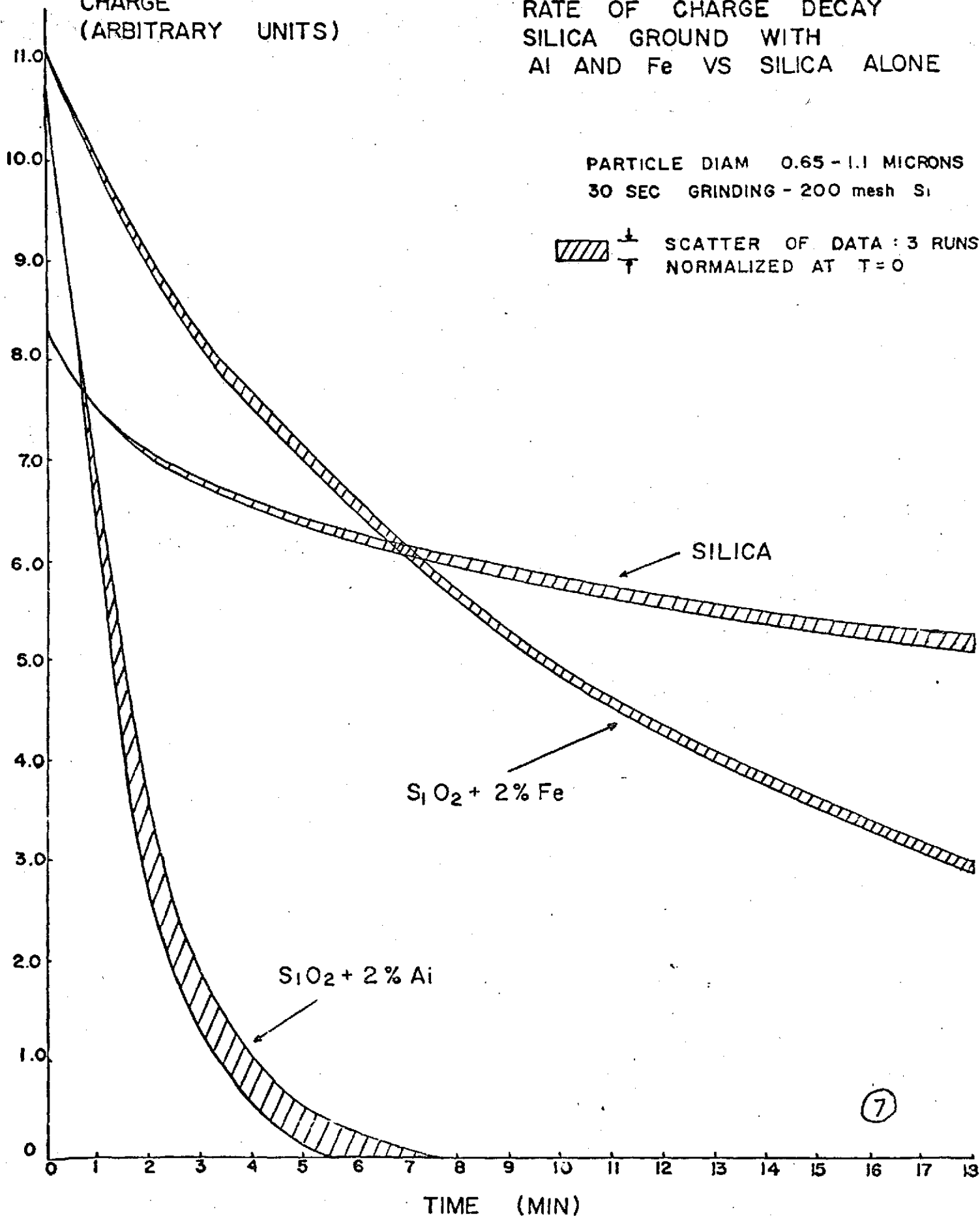


CHARGE
(ARBITRARY UNITS)

RATE OF CHARGE DECAY
SILICA GROUND WITH
Al AND Fe VS SILICA ALONE

PARTICLE DIAM 0.65 - 1.1 MICRONS
30 SEC GRINDING - 200 mesh Si

▨ ± SCATTER OF DATA : 3 RUNS
T NORMALIZED AT T=0



APPENDIX 2

ANALYSIS OF ELECTROSTATIC LEVITATION EFFECTS

DUST LEVITATION CALCULATION

In reference 6, pg. 170, the authors consider the statistical mechanics of a group of particles. Assuming Boltzmann statistics and the perfect gas law, the authors derive the formula

$$N = N_0 \exp (- mgZ/kT)$$

based on the potential $\phi = mgZ$. This formula for the number of particles at a level Z can be used to develop the adiabatic law of the atmosphere

$$P_1 = P_0 \exp (- mgZ/kT)$$

where m , g , k and T have their usual meaning and Z is the altitude.

If we consider a cloud of charged dust particles in an electrostatic field the potential becomes $\phi = mgZ - QnE$. Here Q is the unit charge, n the number of charges per particle and E is the voltage gradient. The $(-)$ sign assumes that the electrostatic forces are opposed to gravity.

Assuming that the field gradient E can be approximated by $E = bZ$ yields a potential of the form

$$\phi = Z (mg - Qnb)$$

If we follow the analysis developed without a field the number density becomes

$$N = N_0 \exp \frac{Z}{kT} (- mg + Qnb)$$

where several constants have been absorbed into N_0 .

The exponential term is clearly the important one in this equation since the magnitude of mg / Qbn will determine the dust density profile. If we calculate the numbers for a 1 micron silica particle we find

$$mg = 1.5 \cdot 10^{-14} \text{ KgM/sec}^2$$

To obtain the value of Qbn we note that $E = 150 \text{ V/M}$ (ref 7) so that $b = 150 \text{ V/M}^2$. This yields a value for $Qbn = 2.4 n \cdot 10^{-17} \text{ cul volts/M}^2$. Any value of "n", the number of charges per dust particle, that makes the ratio

$$\frac{mg}{Qbn} \leq 10$$

will result in significant dust levitation because of Stokes Law effects.

Using the above numbers

$$\frac{mg}{Qbn} = \frac{625}{n}$$

The data of reference 3 indicates that many 1 micron silica particles acquire over 100 electronic charges when blown through a platinum cup. Under these conditions we can expect that significant levitation will occur in the earth's atmosphere.

APPENDIX 3

A SYSTEM FOR METHANE RECOVERY AND FERTILIZER PRODUCTION FROM GARBAGE AND SEWAGE



THE UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

DEPARTMENT OF ELECTRICAL ENGINEERING

May 30, 1974

Mr. Tom Price
City Operations Manager
City Hall
Tucson, Arizona

Dear Mr. Price,

Enclosed please find one copy of our report on the generation of methane (natural gas) from garbage and sewage. You will note that we obtained some 500 cubic feet of gas (55% methane) from about 720 gallons of raw sewage, or 0.7 cubic feet per gallon.

If we extrapolate these figures to the City of Tucson, using 1972 data, we find that the City produced 10^{10} gallons of sewage. This would convert to 3.5×10^9 cubic feet of methane or about 11.5% of the 3.5×10^{10} cubic feet of gas that TGE sold in 1972.

This data is certainly on the conservative side because we have not taken account of any process improvements, the use of garbage, or sewage from Pima County. In view of the above we suggest that production of methane from sewage has significant potential for the City of Tucson.

We appreciate the opportunity to have made this investigation. Your staff, especially Mr. R. Gerhart, have been most cooperative.

Yours Truly

S. J. Greenig
S. J. Greenig
Prof. EE

A SYSTEM FOR METHANE RECOVERY AND
FERTILIZER PRODUCTION FROM GARBAGE AND SEWAGE

Prepared for presentation at the Fourth Annual Composting
Conference, May 1-3, 1974 in El Paso, Texas

by

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The support of the University of Arizona, The City of Tucson, Mr. Roy Burkett, and the Tucson Gas and Electric Company is gratefully acknowledged. Mr. Christian Savitz was of great help in the construction and maintenance of our system.

Abstract

The history of methane generation is reviewed and a discussion of the University of Arizona system is given. We have demonstrated that appreciable quantities of methane can be generated by anaerobic digestion of raw sewage and ground-up garbage.

Introduction

Methane formation is a unique event, confined to a relatively small group of microbes which have morphological representatives among the cocci, bacilli and spirillae^[8]. Despite this uniqueness however, the production of methane is widely distributed in nature, being found in such anaerobic environments as the black muds of swamps and lakes, in coal mines - trapped there during coal formation, in sewage sludge systems, and in the digestive tracts of animals especially ruminants^[8]. It has been reported that in a large cow which may have "100 liters of fermenting plant products in the rumen," that in excess of 200 liters of methane may be produced per day, which amounts to an eight to ten percent energy loss to the cow^[8].

The first reported case of methane production by man was in 1895, when Donald Cameron built the first city-sized septic tank for Exeter, England^[4]. This system removed eighty percent of all solids from the system and earned Cameron the title of "pioneer in his field." The gas from this tank was collected and utilized for street lighting in the vicinity of the plant^[4].

Later two tiered plants were developed, such as the Travis tank at Hampton, England in 1905, and the Imhoff tank in the Emschere district of Germany in 1907^[4]. These tanks provided for a flow through chamber separated from the digestion chamber by baffles thus protecting the effluent from the foul smelling materials produced by anaerobic digestion^[4]. By the mid to late twenties the trend in treatment had turned to a separate digestion chamber for the solids with the acceptance of the Alvord tank^[4].

In these anaerobic digesters carbohydrates, amino acids, proteins, lipids, and other nitrogenous compounds from living cells are broken down to fatty acids, alcohols, carbon dioxide and hydrogen^[3,8], by non-methanogenic bacteria. From these compounds methanogenic bacteria synthesize methane^[3,8]. The main volatile acids produced during anaerobic digestion are acetic, propionic, and butyric acids with lesser amounts of formic and valeric acids^[3]. Propionic and valeric acids have been found to derive from proteinaceous materials^[3].

The first isolation of a methane producing system was in 1916 by Omelanski from rabbit feces in a medium containing one percent ethanol as substrate^[8]. Later Baker isolated a similar system from Delft canal mud and San Francisco Bay mud using an ethanol-carbonate minimal enrichment medium with the name Methanobacterium omelanskii being given to these cultures^[8].

In these cultures two moles of ethanol are oxidized to acetate and the eight moles of hydrogen derived from this process are utilized to convert carbon dioxide to methane. These cultures could also produce methane from carbon dioxide and hydrogen alone, or if ethanol alone is provided, with no carbon dioxide present, the system produces acetate and hydrogen. Further it was found that if a hydrogen atmosphere is provided no acetate is produced by the culture^[8].

In 1965 Bryant and Wolfe cultured M. omelanskii by the Hungate technique in a rich medium containing rumen fluid. From this culture an organism was isolated that was unable to oxidize ethanol but was

able to produce methane from carbon dioxide and hydrogen^[8]. Later Bryant was able to isolate an organism from M. omelanskii which could produce acetate and hydrogen from ethanol but not methane. Thus it was shown that Methanobacterium omelanskii was, in fact, two organisms; the one, able to oxidize ethanol or acetaldehyde to acetate and hydrogen was called "S" organism and possesses both an ethanol dehydrogenase and a formate dehydrogenase requiring NAD for activity, it also requires the removal of hydrogen evolved from NADH via a ferredoxin dependent reaction^[6] from the medium by Methanobacterium strain M. O. H., the second organism, which produces methane from hydrogen and carbon dioxide^[6,7,8].

Natural enrichment of methane bacteria may be accomplished from sewage-sludge, rumen fluid, black muds, or intestinal contents via the Hungate technique; the essential component of which is the complete lack of oxygen^[8]. In this technique roll tubes of the appropriate enrichment medium are prepared using a stream of carbon dioxide and hydrogen, plugged with rubber stoppers, sterilized, and inoculated under a reduced atmosphere of carbon dioxide and hydrogen^[8].

All of the methane bacteria, with the exception of Methanosarcina barkeri, which prefers methanol or acetate, utilize hydrogen and carbon dioxide or formate as their preferred substrate, organisms using propionate, butyrate or higher fatty acids and alcohols are not represented in pure cultures^[8]. Ammonium ions are used as the sole nitrogen source with certain growth factors being required by some species^[8].

Utilizing these substrate sources, continuous culture techniques have been worked out for growing these organisms under anaerobic conditions, giving yields of 50-60 grams wet weight per liter of medium. Growth is slow, requiring about three days to attain log phase growth^[8]. The amount of carbon dioxide utilized equals the amount of methane produced, however, the theoretical carbon to hydrogen ratio of four to one has not been achieved but is instead around 3.7 to one^[8], indicating that a small portion of the reducing power comes from the medium itself. Growth on formate presents problems of pH and gas formation. The medium must be continuously buffered with formic acid to prevent it from becoming alkaline, further four moles of formate are decomposed to produce one mole of methane and three moles of carbon dioxide. Vessel pressures increase which may cause vessel rupture or to blow its cork^[8], causing violent frothing.

M. barkeri has been cultivated in two hundred liter batches yielding fourteen grams of wet weight organisms in seven to fourteen days. These organisms represent the highest levels for mass culture of any methane bacteria to date, however growth on acetate by this organism is very slow^[8].

The physiology of these organisms has been studied extensively to date using cell suspensions or cell free extracts^[1,6,7,8,9] in modified Warburg flasks flushed with mixtures of carbon dioxide and hydrogen, gas samples being removed via hypodermic syringe for analysis in^A gas chromatograph. However, to prevent prolonged lag in the reaction rate the suspending buffers must be free of oxygen and exposure of these cells must be kept to a minimum.

Using cell free extracts the first substrate found to be active in methane formation was pyruvate via the carboxyl group with free carbon dioxide as the intermediate^[8]. The intermediary steps from carbon dioxide to methane are not as yet understood since no intermediates have been isolated. However, synthesis seems to be membrane bound as postulated by Zeikus and Wolfe^[9] and that a certain reductive co-factor (F420)-enzyme association is a general requirement for the preservation of certain catalytic sites in these fastidious non-spore forming anaerobes^[1].

Further, the formation of methane requires not only hydrogen but ATP as well. A linear and direct relationship exists between ATP and methane production^[8], however once ATP is added further ATP is no longer required, therefore its action appears catalytic^[8]. In addition to this, magnesium ions, vitamin B₁₂ and a co-enzyme M, found only in methane bacteria, are required for synthesis. The proteins associated in methane production include ferredoxin, a carrinoid protein and an as yet unidentified protein X^[8].

As was stated previously, the methane bacteria are the most sensitive of all organisms to oxygen. It has been suggested by Cheeseman, et al.,^[1] that this sensitivity is due to a reductive co-factor involved in NADPH reduction which dissociates from its enzyme association in the presence of oxygen^[1]. Uncouplers of oxidative phosphorylation also inhibit methane production^[8], chloroform and carbon tetrachloride serve as competitive inhibitors reacting with B₁₂^[8]. Nitrate and sulfate also serve as inhibitors in methane formation though the mechanism is not well understood^[4].

A number of groups, in and out of the United States, are investigating the generation of methane from garbage and sewage materials. A copy of the program of the El Paso meeting is attached to this report as an appendix. It will indicate the organizations and topics involved.

Experiments at the University of Arizona

The use of these organisms for the production of methane from sewage presents some unique problems. Initially the decision was made to use a batch load digester. An elevation of the digester is attached as Figure 1. The chamber measures seven feet in diameter and four feet deep and is painted black for heat absorption. It is equipped with a carbon dioxide aeration device, a temperature probe and recorder, a gas meter to measure flow rates and obtain gas samples, a calorimeter to measure heat capacity and a sampling well from which pH, buffering capacity, volatile acids, chemical oxygen demand (COD) as total carbon sulfate and nitrate may be determined.

Initially the tank was buried in the ground with the hope that the exothermic heat of decomposition would raise the temperature to the proper operating level of 30°C (80°F). This did not prove to be the case, primarily because the sewage level was 1 1/2 feet below the exposed cover.

To overcome this problem, a solar heater made of 100' of 1 inch plastic pipe was obtained and a circulating pump was added to the system to move the liquid thru the pipe. This pumping action helped mix the slurry in the digester. The pump and heater increased the temperature

ten degrees centegrade from twenty to thirty degrees in nine days. The COD was also found to rise, probably due to more complete mixing.

The batch digester was loaded to a capacity of 720 gallons with a ratio of seven to one, volume to weight, with sewage-sludge and garbage. The pH range of our system ranged, to date, between 6.8 to 7.7 with one peak at 10.3 after the addition of fifty pounds of lime to reduce volatile acid concentrations. The buffering capacity of the system ranged between 1780 ppm to 3020 ppm titrated to pH 4.5^[5] as determined on the Hatch DR-EL direct reading portable Engineer's Laboratory.

Volatile acids ranged from forty-eight mg/l to 3722 mg/l. Lime was added initially to decrease volatile acids but was found to increase pH unacceptably. The addition of carbon dioxide to the system depressed pH while increasing both COD and volatile acids.

Nitrates were found to be at levels too low to affect methane production (6 ppm), however, sulfates, at 325 ppm, were found to be unacceptably high, and methane production did not initiate until their level dropped below 100 ppm. Tap water in the Tucson area was found to contain 140 ppm sulfate and sewage had 250 ppm indicating that sulfates will continue to be a problem in a continuous flow digester.

Operational parameters for the system were arranged to provide the proper pH and volatile acid level. The optimum pH range for methane production is between 6.4 and 7.2, below pH 6.0 and above 8.0 methane production declines rapidly^[3]. The buffering capacity of the

system must also be measured to determine the system's resistance to pH change^[3]. Concentrations of volatile acids should be maintained between 100 and 300 mg/l (as acetic acid) for optimum digestion, concentrations above 2000 ppm cause a total collapse of the system. In general, a rapid rise in volatile acids indicates impending collapse of the system^[2,3,4].

Reduction of volatile acids may be achieved by addition of lime, which will also increase the buffering capacity, however, ammonium bicarbonate is somewhat superior to lime in that it may also serve as a substitute source for the system^[3]. Carbon dioxide was found to increase volatile acids and depress pH to an unfavorable degree. Further, the ratio of methane to carbon dioxide should be measured since it is as important a parameter as the gas volume itself. (Any decline in the rate of gas production, from a constant value accompanied by a change in the methane to carbon dioxide ratio, is indicative of unbalanced conditions and preceeds an increase in volatile acids by twenty-four hours^[3].) The pH of the samples were measured on a Leeds and Northrup pH meter; and volatile acids measured via Standard Methods^[5].

The COD via the dichromate reflux method in Standard Methods^[5] appears to be the most favored method for expressing the amount of oxidizable material contained in waste^[3]. Nitrates and sulfates were measured as inhibitors to methane production^[4] via the Hatch DR-EL process.

The gas itself was periodically analyzed by bringing samples to a mass spectrometer. The analyses were done by Mr. Godfrey Sill of the University of Arizona Lunar and Planetary Laboratory, his assistance is gratefully acknowledged. Typical composition percentages were: Methane, 55 percent; Nitrogen (N_2 gas), 35 percent; Carbon Dioxide, 18 percent; Sulfur Dioxide, Hydrogen Sulfide and Hydrogen gas at much less than one percent as determined on a mass spectrometer. Gas production continued for some 50 days with a total measured output of 500 cubic feet. This does not account for gas lost during modifications and necessary opening of the reaction tank. During the gas production cycle we observed a significant drop-off in both COD and volatile acids. The changes in these parameters over an 80 day period are shown in the attached Figure 2.

CONCLUSIONS AND PROPOSED FUTURE STUDIES

The results, from this somewhat primitive study, indicate that significant quantities of combustible gas can be obtained from a mixture of raw sewage and garbage.

Future plans involve the use of a continuous-flow digester supplied with a mixture of ground garbage and sewage-sludge fed into a large pit lined and covered with Hypalon and equipped with float hoses for the collection of gases. A schematic of the proposed system and layout of a typical digestion system are shown in Figures 3 and 4.

In view of our high sulfate values it might be feasible to add a pre-chamber with a 2-day retention time to the system. The chamber would be seeded with Desulfovibrio sp. to eliminate sulfates as hydrogen sulfide gas before the slurry is allowed to enter the digester proper. Further, the feed slurry should be concentrated to a total carbon content, as COD, of 10,000 - 20,000 parts per million carbon^[2] instead of its current average of 1,000 milligrams per liter carbon. This will significantly enhance methane gas production.

With a continuous-flow system the need for daily monitoring of volatile acids, gas production, carbon/nitrogen ratios, buffering capacity and pH will become essential. Later, when the continuous-flow digester system becomes large enough it may become feasible to run a small laboratory model plant using seed stock from the digester and the proposed feed mixture to determine whether the sewage-garbage mixture contains inhibitors to methanogenesis before it is fed into the digester. This modification will necessitate the addition of a twenty-four hour holding chamber placed after the aforementioned pre-chamber to hold the feed stock until it has been found clear of inhibitors (24 hours).

As to the gas produced by anaerobic digestion, after collection it may be passed through a basic solution of sodium hydroxide or preferably ammonium hydroxide where the carbon dioxide will be removed as its respective carbonate and may in this state be utilized to increase buffering capacity and provide additional feed stock.

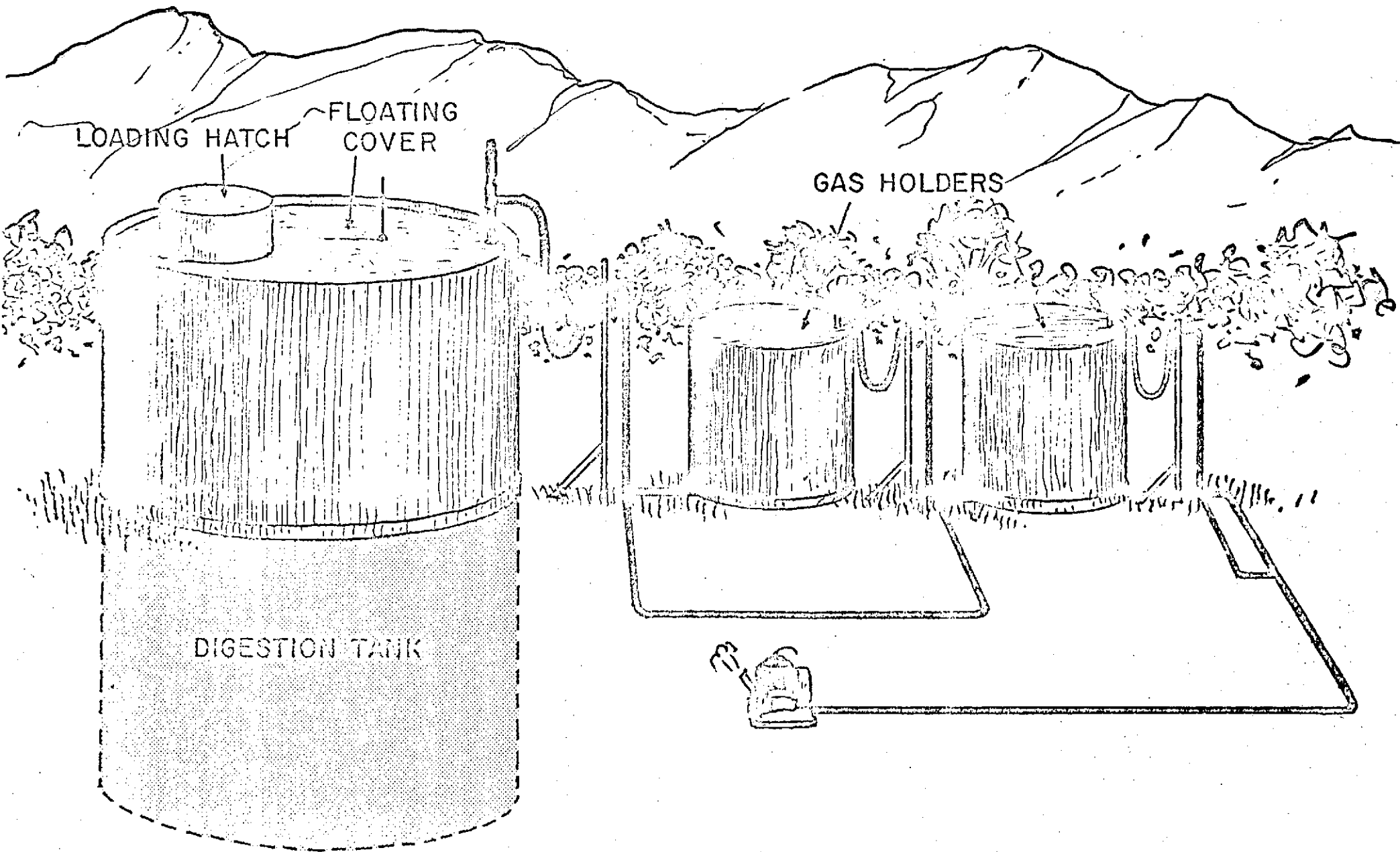
The sludge from the digester has commercial value as a fertilizer and could be used to augment the cost of operation for the plant. The

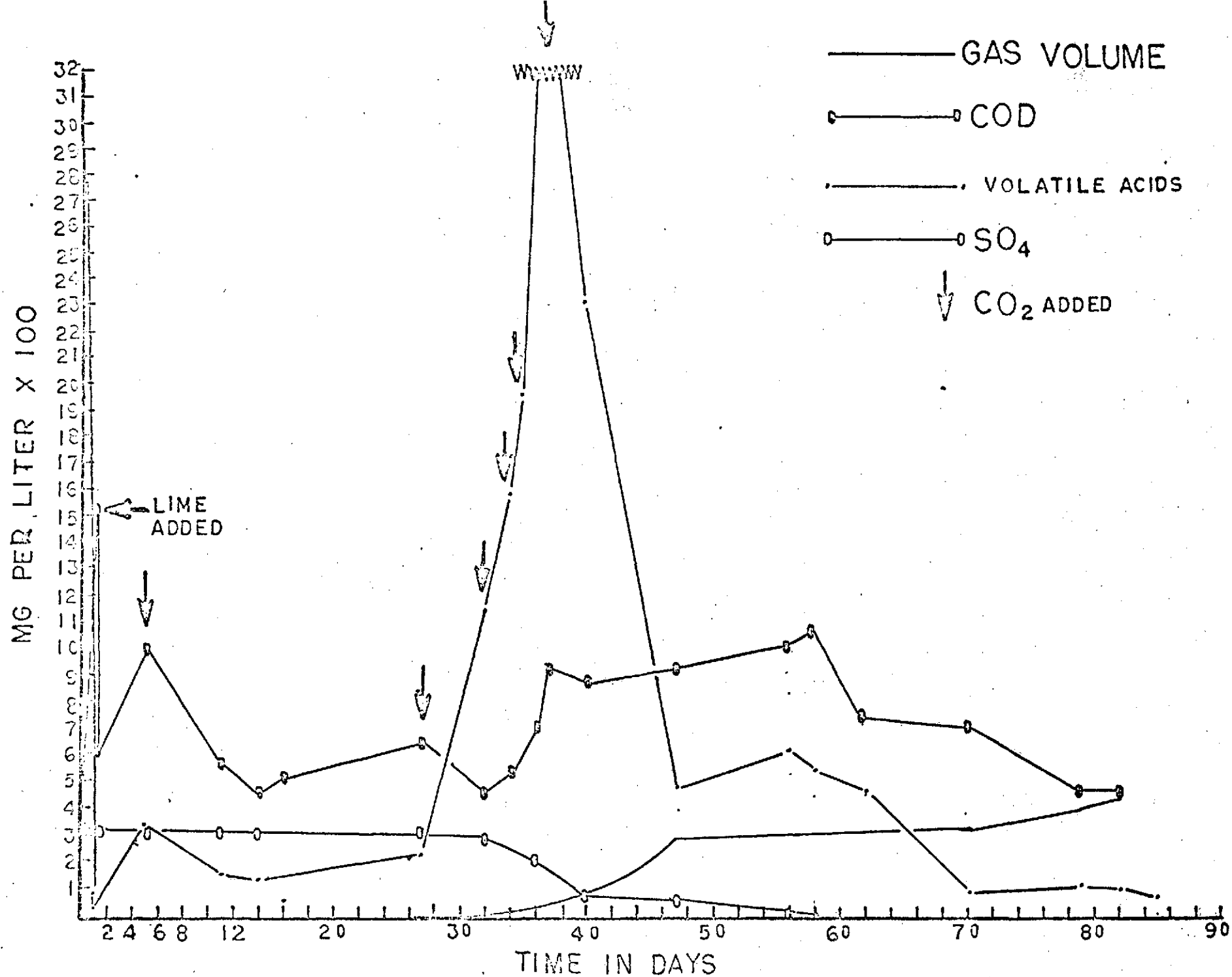
liquid effluent could be used for agriculture if some minor additional treatment is provided.

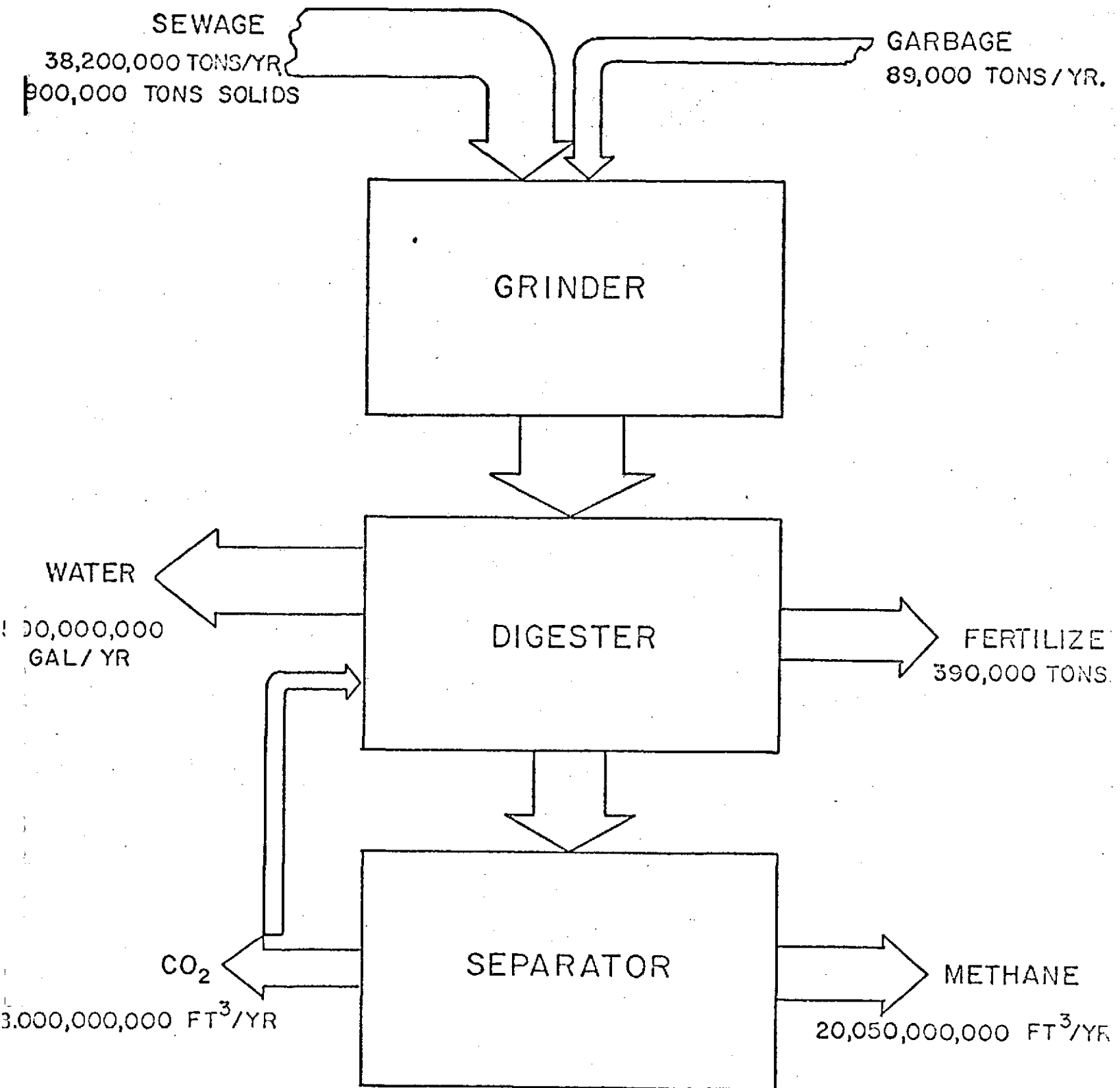
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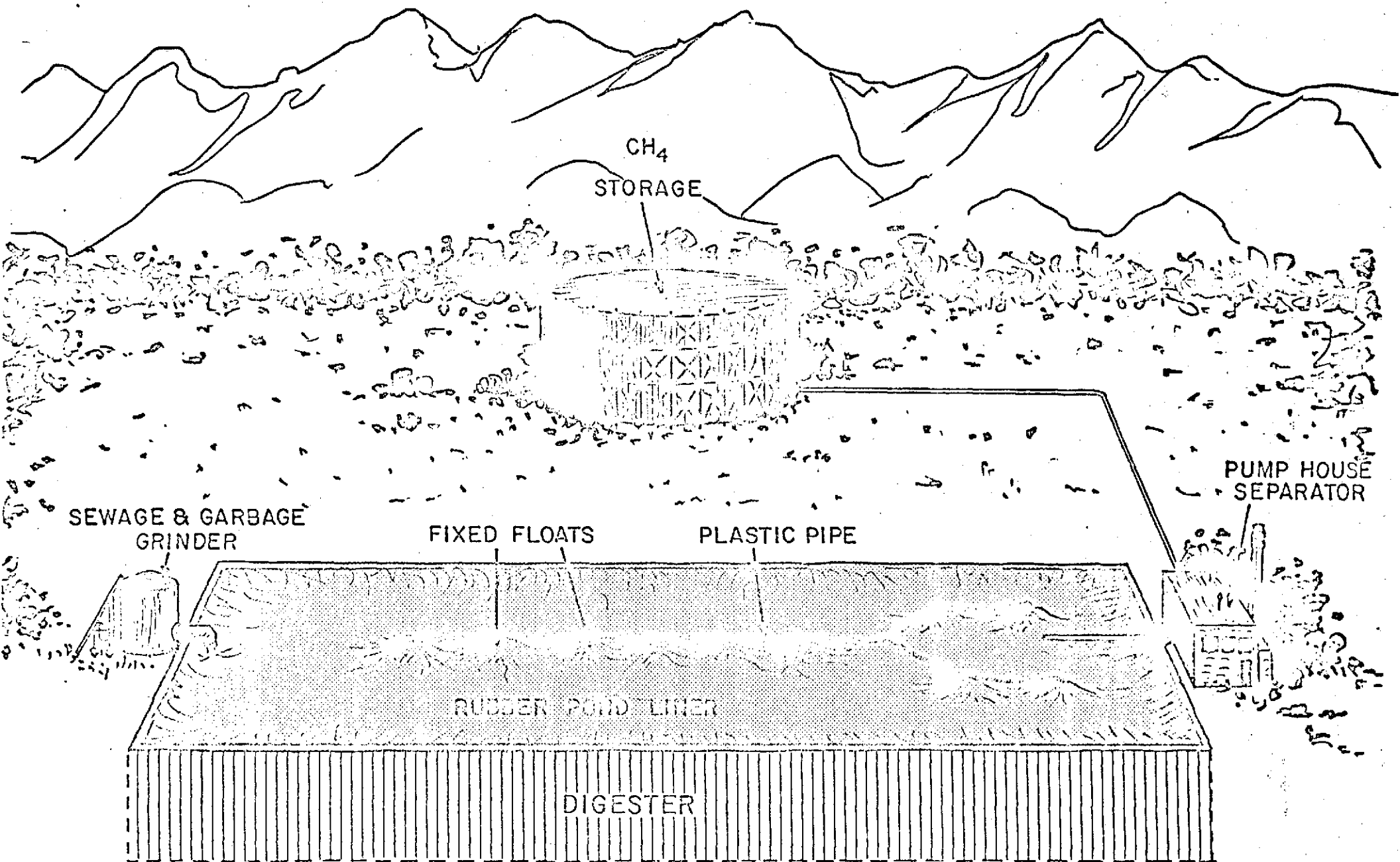






FIGURES

- 1) Schematic Drawing of the Digestion System
- 2) Gas Volume, COD, Volatile Acids and SO_4 from the Reaction Tank
Over An 80 Day Period
- 3) Schematic Arrangement of the Proposed Digestion System
- 4) Elevation Drawing of the Proposed Digestion System



APPENDIX: PROGRAM FROM THE COMPOSTING AND WASTE RECYCLING CONFERENCE
May 2-3, 1974, El Paso, Texas

~~Industrial Waste~~ John M. Sweeten, President
Mechanical Consultants, Inc., El Paso, Texas

Combining Municipal Waste With Feedlot Manure—
John M. Sweeten, Agricultural Engineer, Texas
A & M University, College Station

—QUESTIONS—

EL PASO, MAY 2, 1974

8:00 AM - 9:00 AM

Composting: Putting Principles Into Practice

Dr. Raymond Poincelot, Connecticut Agricultural
Experiment Station, New Haven, Conn., Biochemistry

Composting Feedlot And Dairy Manure

Charles L. Serna, School of Public Health, University of
California, Los Angeles

**Equipment For Incorporating Biodegradable Wastes Into The
Soil**

Martin Decker, Dept. of Agricultural Engineering, Rutgers
University, New Brunswick, N.J.

Organic Farming And Marketing

Frank Ford, President, Arrowhead Mills, Hereford, Texas

—QUESTIONS—

—DISCUSSION—

LUNCH

AFTERNOON SESSION 1:45 p.m.

Energy Expenditure And Food Production

Richard Whitman, Cornell University

A Composting Process For Small Communities

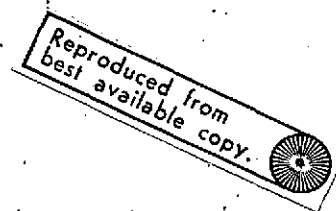
Zoeil Colburn, Ambassador College, Big Sandy, Texas

Recycling Municipal, Industrial And Agricultural Wastes

Geoffrey Stanford, President, Agro City Planning Consul-
tants, Austin, Texas

—DISCUSSION—

CONFERENCE SUMMARY



COMPOSTING

WASTE MANAGEMENT

MAY 2-3, 1974 EL PASO, TEXAS

Sponsored by
RODALE PRESS, INC.
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Karen Jones, Information Service
New Mexico State University

RODALE PRESS

Marlene Fray
Jerome Goldstein
Clarence Goluske
Mildred Lutz

May 13, 1974

All conference sessions, luncheons and meetings will be held at:
Sheraton El Paso Motor Inn, 4151 N. Mesa, Highway 80-85-180
West, El Paso.

WEDNESDAY, MAY 1, 1974—8:00 p.m. to 10:30 p.m.

Pre-Registration and Get-Together

Films: "Composting"
"Wealth from Wastes"
"The Living Filter"
"Looking for Organic America"

THURSDAY, MAY 2, 1974

8:00 a.m. to 9:00 a.m.—Registration

MORNING SESSION

Where We Are Today In Composting And Recycling
Maurice Franz, Managing Editor, Rodale Press

Biological Reactions In Waste Recovery Systems
Clarence Golueke, Sanitary Engineering Research Lab.,
University of California

Methane Gas Production Is Part Of A Recycling System
Luis Diaz, Department of Mechanical Engineering,
University of California

Perpetual Methane Recovery
Raul Zaitzman, Department of Civil Engineering, West
Virginia Univ.

Design For Methane Recovery And Fertilizer Production System
In Tucson, Ariz.
Stuart Heenig, Department of Electrical Engineering,
University of Ariz.

A Small Town Turns To Composting And Recycling
Robert E. Reid, Councilman, Brookhaven, New York

—DISCUSSION—

AFTERNOON SESSION 1:45 p.m.

Where We Would Like To Be In Composting And Recycling
Jerome Goldstein, Executive Editor, Rodale Press

Chicago's Prairie Plan—Why Does It Work And What Does It
Mean To Other Cities?
Frank Kudrna, Eng. of Planning, Chicago Metro Sanitary Dis.

Political Aspects Of Composting Vs. Landfill
Anthony Nolle, President, All-American Env. Control
Corp.

Composting And Waste Recycling In Mexico
Joaquin Tello, Dept. of Health, Education and Welfare,
Sanitary Eng. Branch, Mexico City

Evaluating Benefits Of Applying Sludge Onto Farmland
Ken Dotson, Research Soil Scientist, Ultimate Disposal
Research Program, EPA, Cincinnati, Ohio

Composting Sewage Sludge—Second Year Report
John Walker, George Willson, Elliot Epstein, Agriculture
Research Service, Beltsville, Maryland

Panel Discussion:

Developing Guidelines
Social Factors
Economic Factors
Environmental Factors
Political Factors

—QUESTIONS—

EVENING SESSION 8:00 p.m.

The Southwest Looks At Composting And Waste Recycling —
With Emphasis on Fuel and Energy Production

Moderator: R. L. York, REERIO, V.P. of Education;
Sr. V.P. of El Paso Electric Company, El Paso, Texas

Municipal Waste—Joseph Pierce, Program Mgr., Solid
Waste Management Section, New Mexico
Improvement Agency, Santa Fe, New Mexico

Agricultural Waste—Charles M. Hohn, Extension
Agricultural Engineer, New Mexico State Uni-
versity, Las Cruces, New Mexico